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Proposed Sampling and Analytical Methodologies for Addition to Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846, 2nd Edition)

(U.S.) Environmental Protection Agency
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1984

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National Technical Information Service
NTIS

PB85-103026

PROPOSED

SAMPLING AND ANALYTICAL METHODOLOGIES

FOR ADDITION TO

TEST METHODS FOR EVALUATING SOLID WASTE
Physical/ Chemical Methods
SW-846
2nd Edition

U.S. Environmental Protection Agency
Office of Solid Waste
1984

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Proposed Sampling and Analytical Methodologies for Addition to "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846, 2nd Edition). A compilation of sampling and analysis methods is being proposed for addition to EPA's methods manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods." Proposed analytical methods include various techniques to characterize samples of waste, groundwater, and stack emissions for properties such as organic and inorganic content, corrosivity, radioactivity, and total oil and grease. Methods are also proposed for sampling groundwater, incinerators and land treatment facilities.

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1.2.1.8 Modified Method 5 Sampling Train

Applicability

This method is applicable to the determination of destruction and removal efficiency from incineration systems. This method also may be used to determine particulate emission rates from stationary sources as per U.S. EPA methodology.

Sampling Train

A schematic of the sampling train used in this method is shown in Figure 1.2.1.8. This sampling train configuration is adapted from EPA Method 5 procedures and as such, the majority of the required equipment is identical to that used in Method 5 determinations. The new component required is the organic module, which is used to collect semi-volatile organic materials that do not condense in the high efficiency fiber filter section.

Construction details for the basic train components are given in APTD-0581 (Citation 2); commercial models of this equipment are also available. Specifications for the organic module are provided in the following subsections. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein, unless otherwise specified. The sampling train consists of the following components:

Probe Nozzle

Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be 30° C and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be the button-hook or elbow design. The nozzle shall be constructed from seamless tubing.

A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Section 5.

Probe Liner

Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature of 120 $\pm$ 14° C (248$\pm$25° F) at the exit end during sampling. (The tester may opt to operate the equipment at a

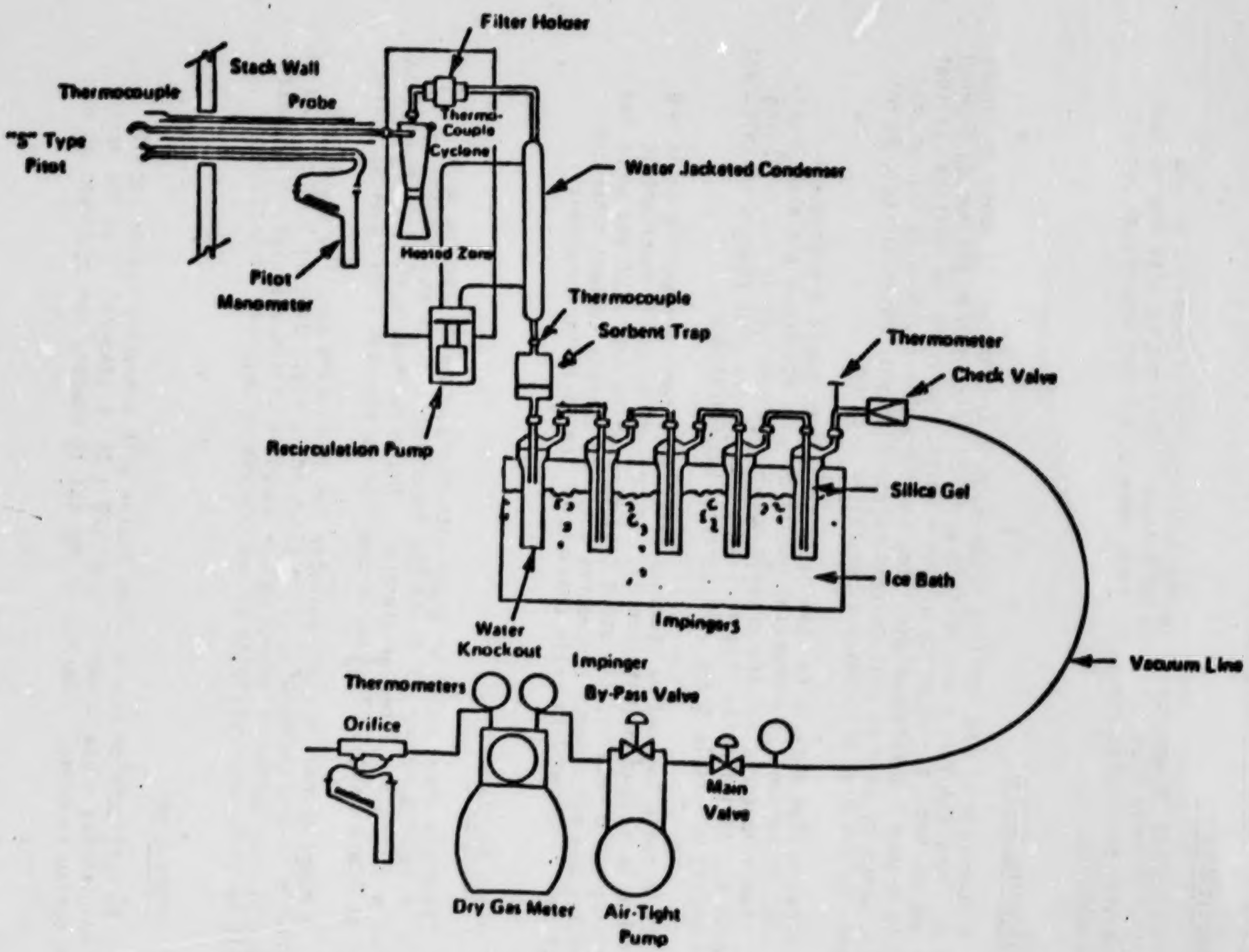
Filter Holder
Stack Wall
Thermocouple
Probe
"S" Type Pitot
Thermo-Couple
Cyclone
Water Jacketed Condenser
Heated Zone
Pitot Manometer
Thermocouple
Sorbent Trap
Thermometer
Check Valve
Recirculation Pump
Silica Gel
Ice Bath
Water Knockout
Impingers
Impinger By-Pass Valve
Vacuum Line
Thermometers
Orifice
Main Valve
Dry Gas Meter
Air-Tight Pump

Figure 1.2.1.8 - 1. Modified Method 5 train.

temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either boroxilicate or quartz glass probe liners may be used for stack temperatures up to about 480° C (900° F). Quartz liners shall be used for temperatures between 480 and 900° C (900 and 1,650° F). The softening temperature for borosilicate is 820° C (1,508° F), and for quartz it is 1,500° C (2,732° F).

Filter Holder

Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of materials which will not introduce organic material into the gas stream at the temperature that the filter holder will be maintained. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

Filter Heating System

Any heating system capable of maintaining a temperature of 120 + 140° C (248 ± 24°F) around the filter holding during sampling. AlternativeTy, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3° C (5.4° F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

Organic Module

A unit consisting of three sections including a gas conditioning section, a sorbent trap and a condensate knockout trap. The gas conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature of 17° ± 3° C (62.5 ± 5.4° F). The sorbent trap shall be sized to contain approximately 40 grams of porous polymeric resin (Rohm and Haas XAD-2 or equivalent), and shall be jacketed to maintain the internal gas temperature of 17 ± 3° C (62.5 ± 5.4° F). The condensate knock-out trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate formed vertically downward from the conditioning section, through the adsorbent media, and into the condensate knockout trap. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, teflon or other inert materials.

Commercial versions of the complete organic module are not currently available, but may be assembled from commercial available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 1.2.1.8-2 and 1.2.1.8-3.

Condensor

The following system shall be used to determine the stack gas moisture content; four impingers connected in series with leak-free ground glass fitting or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 in) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water (Preparation of Collection Train), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1° C(2° F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condensor each to within 1 ml or 1 g may be used. Acceptable methods are to measure the condensed water either gravimetrically or volumetrically and measure the moisture leaving the condensor by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20° C (68° F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) shall be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

Metering System

Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than described in APTD-0581 and APTD-0516 may be used provided that the specifications of this method are met.

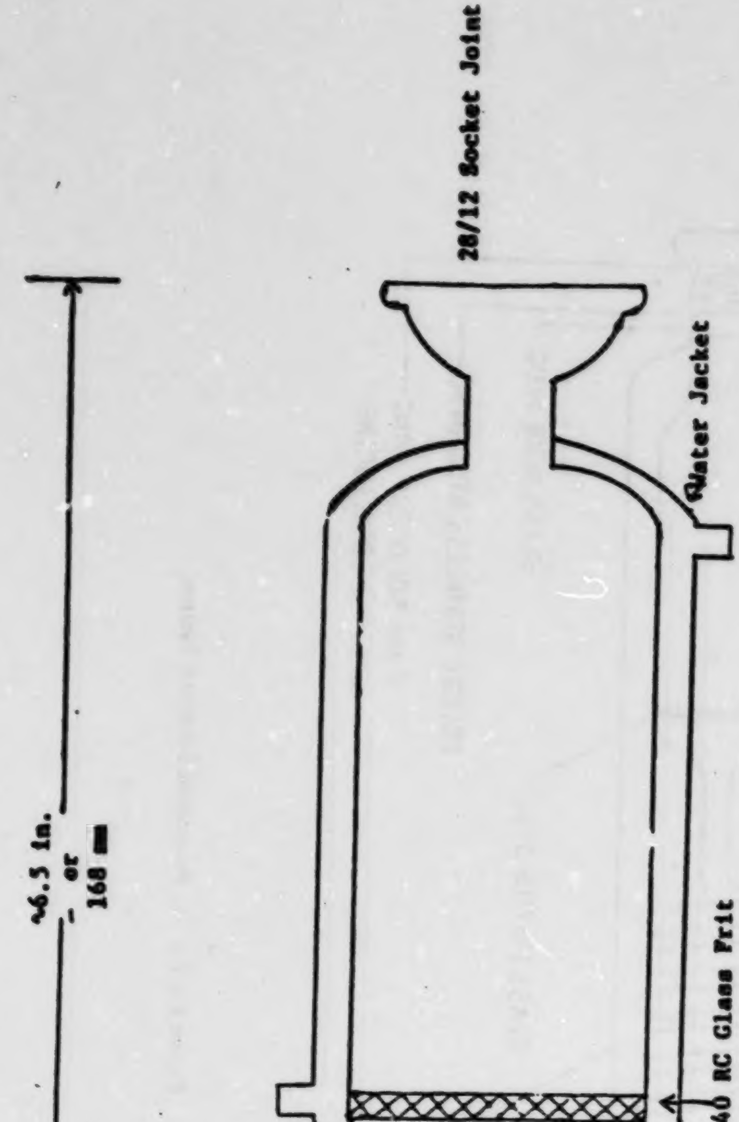
28/12 Socket Joint
Water Jacket
40 RC Glass Frit
~6.5 in. or 168 mm
28/12 Ball Joint
~1-11/16" or 45 mm

Figure 1.2.1.8 - 2. Absorbent Sampling System.

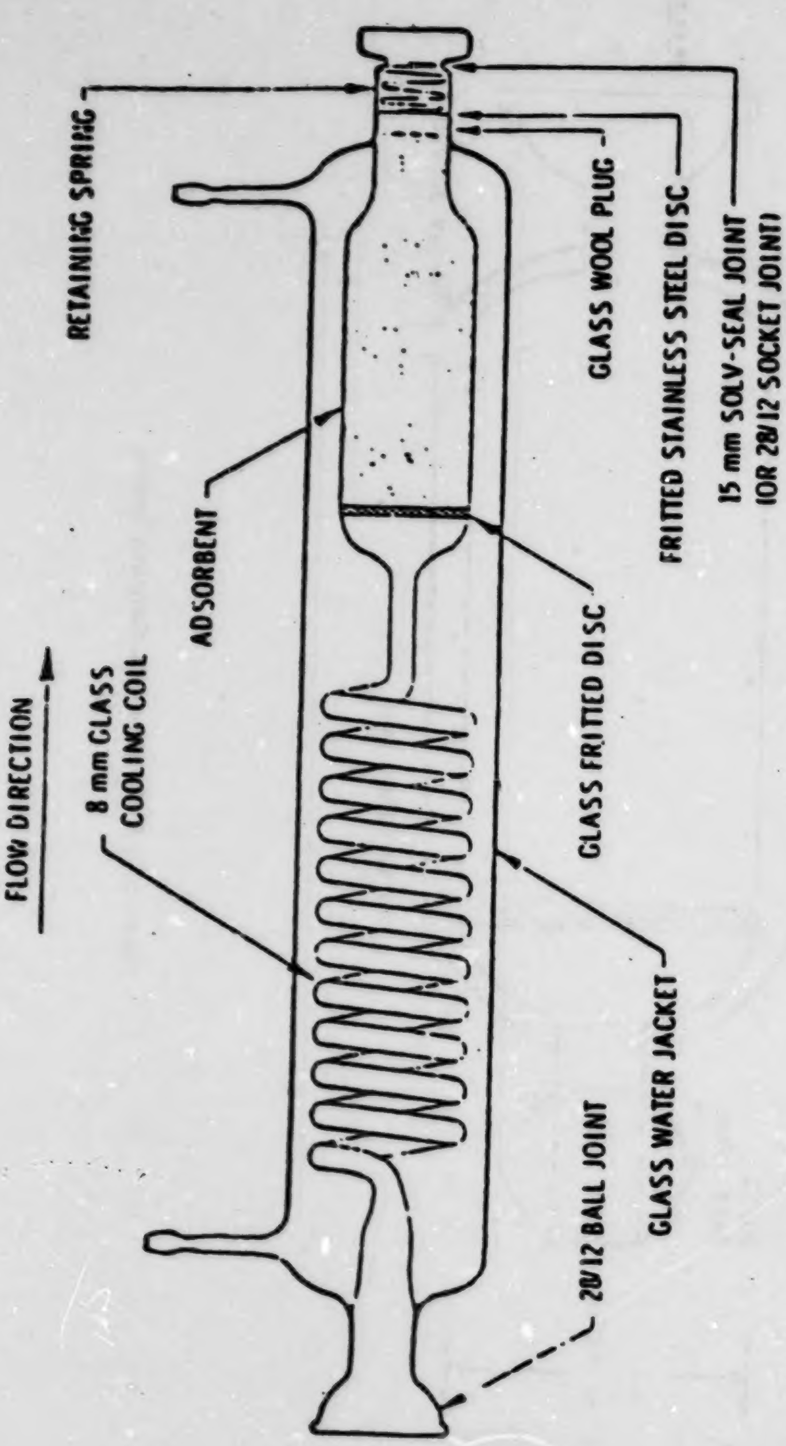
RETAINING SPRING
GLASS WOOL PLUG
FRITTED STAINLESS STEEL DISC
15 mm SOLV-SEAL JOINT
(OR 28/12 SOCKET JOINT)
ADSORBENT
GLASS FRITTED DISC
FLOW DIRECTION
8 mm GLASS
COOLING COIL
GLASS WATER JACKET
28/12 BALL JOINT

Figure 1.2.1.8 - 3. Adsorbent Sampling System.

Barometer

Mercury aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.5 in. Hg). In many cases the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

Gas Density Determination Equipment

Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of 40 CFR 60 Method 2, and gas analyzer, if necessary as described in 40 CFR 60 Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see 40 CFR 60 Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

Sample Recovery

The following items are needed.

Probe-Liner

Probe-Nozzle and Organic Module Conditioning Section Brushes-Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Teflon, or inert material. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle and the organic module conditioning section.

Wash Bottles

Three. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used as organic contaminents may be extracted by exposure to organic solvents used for sample recovery.

Glass Sample Storage Containers

Chemically resistant, borosilicate glass bottles, 500 ml or 1,000 ml. Bottles should be tinted to prevent action of light on sample. Screw cap liners shall either be Teflon or shall be constructed so as to be leak free and resistant to chemical attack by organic recovery solvents (narrow mouth glass bottles have been found to exhibit less tendency toward leakage).

Petri Dishes

Glass sealed around the circumference with Teflon tape, for storage and transport of filter samples.

Graduated Cylinder and/or Balance

To measure condensed water to the nearest 1 ml of 1 gram. Graduated cylinders shall have subdivisions no greater than 2 ml. Laboratory triple-beam balances are capable of weighing to ±0.5 gram or better.

Plastic Storage Containers

Air-tight containers to store silica gel.

Funnel and Rubber Policeman

To aid in transfer of silica gel to container; not necessary if silica gel is weighed in field.

Funnels

Glass, to aid in sample recovery.

Reagents and Materials

Sampling

The reagents used in sampling are as follows:

Filters

A filter is not a reagent. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on

0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program are sufficient for this purpose. In sources containng SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Citation 10 in Section 7 may be used to select the appropriate filter.

Adsorbent Resin

Porous Polymeric Resin (XAD-2 or equivalent) is recommended. These resins shall be cleaned prior to their use for sample collection. Manufacturers' literature should be consulted to determine appropriate precleaning procedure. For best results, resin used should not exhibit a blank of higher than 4 mg/kilogram of Total Chromatographiable Organics (TCO) prior to use. Once cleaned, resin should be stored in sealed container to limit exposure to ambient air.

Silica Gel

Indicating type, 6 to 16 mesh. If previously used, dry at 175° C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

Impinger Solutions

Distilled water shall be used, unless sampling is intended to quantify a particular inorganic gaseous species. If sampling is intended to quantify the concentration of additional species, the impinger solution of choice shall be subject to Administrator approval.

Crushed Ice

Stopcock Grease

Solvent-insoluble, heat stable silicone grease. Use of silicone grease upstream module is not permitted and amounts used on components located downstream of organic module shall be minimized. Silicone grease usage is not necessary if screw-on connectors and Teflon sleeves or ground glass joints are used.

Glasswool

Sample Recovery. The following reagents are used during sample recovery.

Methylene Chloride. Methylene Chloride-distilled in glass grade is required.

Methyl Alcohol. Methyl alcohol distilled in glass grade is required. Note. Organic solvents from metal containers may have a high residue blank and should not be used. Sometimes, suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with low blank value (≤0.001 percent) shall be used.

Water. Distilled water shall be used for rinsing the organic module and condenser component.

Procedure

Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

Pretest preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20 ± 5.6° C (68 ± 10° F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., less than 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere and a relative humidity above 50 percent for a period greater than 2 minutes. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed.

Preliminary Determinations

Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2.

It is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6. If integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

A minimum of three (3) dscm (105.9 dscf) of sample volume is required for this determination. Additional sample volume shall be collected as necessitated by analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 6.

Determine the total length of sampling time needed to obtain the identified minimum volume, by comparing the anticipated average sampling rate to the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. It is recommended that the length of time sampled at each traverse point be an integer or an integer plus one half minute to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

Preparation of Collection Train

During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Fill the sorbent trap section of the organic module with approximately 40 grams of clean adsorbent resin. While filling, insure that the trap packs uniformly to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, which will cause clinging to trap walls. This may be minimized by filling the trap in the presence of an antistatic device.

If an impinger train is used to collect moisture, place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260° C (500° F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack of duct for each sampling point.

Set up the train as in Figure 6. During assembly, do not use any silicone grease on ground glass joints that are located upstream of the organic module. A very light coating of silicone grease may be used on all ground glass joints that are located downstream of the organic module, but should be limited to the outer portion (See APTD-0576) of the ground glass joints to minimize contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack. Organic module condenser must be maintained at a temperature of 17 ± 3° C.

Place crushed ice around the impingers and the organic module condensate knockout.

Leak-Check Procedures

Pretest leak-check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 280 mm Hg (15 in. Hg) vacuum.

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 280 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with rest of the sampling train, in one step at 380 mm Mg (15 in Mg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass value; this will cause water to back up into the organic module. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the organic module and silica gel from being entrained backward into the third impinger.

Leak-checks during sampling run. If during the sampling run, a component (e.g., filter assembly, impinger or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in "Pretest leak-check" above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in the calculation section of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in pretest leak-check above shall be used.

Post-test leak-check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in pretest leak-check, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in the calculation section of this method or shall void the sampling run.

Sampling train operation. During the sampling run, maintain an isokinetic sampling rate to within 10 pecent of true isokinetic unless otherwise specified by the Administrator. Maintain a temperature around the filter of 120 ± 14° C (248 ± 25° F) and a gas temperature entering the sorbent trap at 17 ± 3° C (62.5 ± 5.4° F).

For each run, record the data required on a data sheet such as the one shown in Figure 1.2.1.8-4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 1.2.1.8-4 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above ranges, do not use the nomographs unless appropriate steps (see Citation 7) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the organic module. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder and the organic module at the proper levels; add more ice, and, if necessary, salt to maintain a temperature of less than 20° C (68° F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. It is recommended that another complete filter/sorbent trap assembly be used rather than attempting to change the filter/sorbent trap itself. Before a new filter/sorbent trap assembly is installed, conduct a leak-check (see leak checks during sampling run). The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

Note that when two or more trains are used, separate analysis of the front-half (if applicable) organic module and impinger (if applicable) catches from each train shall be performed, unless identical nozzle sizes were used on all trains, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in post-test leak-check. Also, leak-check the pitot lines as described in Method 2. The lines must pass this leak-check, in order to validate the velocity head data.

Calculation of percent isokinetic. Calculate percent isokinetic (see Calculations below) to determine whether the run was valid or another test run should be made.

Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

Plant____________________

Location____________________

Operator____________________

Date____________________

Run No.____________________

Sample Box No.____________________

Meter Box No.____________________

Meter ΔH@____________________

C Factor____________________

Pitot Tube Coefficient C_p__________

Schematic of Stack Cross Section

Ambient Temperature____________________

Barometric Pressure____________________

Assumed Moisture %____________________

Probe Length, m (ft)____________________

Nozzle Identification No.____________________

Average Calibrated Nozzle Diameter, cm(in)____

Probe Heater Setting____________________

Leak Rate, m^3/min, (cfm)____________________

Probe Liner Material____________________

Static Pressure, mm Hg (in.Hg)____________________

Filter No.____________________

Traverse Point Number	Sampling Time (θ).min.	Vacuum mm Hg (in.Hg)	Stack Temperature (T_S) °C(°F)	Velocity Head (ΔP_S). mm(in)H_2O	Pressure Differential Across Orifice Meter mm(H_2O) (in H_2O)	Gas Sample Volume m^3 (ft^3)	Gas Sample Temp. At Dry Gas Meter		Filter Holder Temperature °C(°F)	Temperature of Gas Entering Sorbent Trap °C(°F)	Temperature of Gas Leaving Condenser or Last Impinger
							Inlet °C(°F)	Outlet °C(°F)			
Total							Avg.	Avg.			
Average											

Figure 1.2.1.8 - 4. Particulate Field Data.

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When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

Cap the filter holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas conditioning section. Cap all organic module openings. Disconnect the organic module knockout trap from the impinger/condensor train inlet and cap both of these openings. Ground glass stoppers, teflon caps or serum caps may be used to seal all openings.

Transfer the probe, the filter, the organic module components, and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

Save a portion of all washing solutions (methanol/methylene chloride, distilled deionized water) used for cleanup as a blank. Transfer 200 ml of each solution directly from the wash bottle being used and place them in separate prelabeled glass sample containers.

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair or pairs of tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with methanol/methylene chloride (1/1 v/v) and placing the wash in a glass container. Distilled water may also be used and a water blank saved. Follow the Administrator's directions on analysis. Perform rinses as follows.

Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1/1 v/v methanol/methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles then make a final rinse of the inside surface with the solvent mix. Brush and rinse the inside parts of the Swagelok fitting with the solvent mix in a similar way until no visible particles remain.

Rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A funnel (glass) may be used to aid in transferring liquid washes to the container. Follow the solvent rinse with a probe brush. Hold the probe in an inclined position, and squirt solvent into the upper end as the probe brush is being pushed with a twisting action through the probe; place a sample container underneath the lower end of the probe, and catch any solvent and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with solvent, and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe as described above:

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with methylene chloride/methanol mixture. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all solvent washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that solvent will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment. If the sorbent trap itself is used as the transport container, both ends should be sealed with tightly fitting caps or plugs. Ground glass stoppers or teflon caps may be used. The sorbent trap should then be labeled and packaged for transport to the laboratory.

If a separate bottle is used, the spent resin should be quantitatively transferred from the trap into the clean bottle. Resin that adheres to the walls of the trap should be recovered using a policeman or spatula and added to this bottle.

Container No. 4. Meaure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 ml using a graduated cylinder or by weighing to within ±0.5 g using a balance. Record the volume or weight of liquid present, and note any discoloration or film in the liquid catch. Transfer this liquid to a prelabeled glass sample container. Inspect the back half of the filter housing, and the gas conditioning section of the organic module. If condensate is observed, transfer it to a graduate or weighing bottle and measure the volume as described above. Add this material to the condensate knockout trap catch.

Container No. 5. All sampling train components located between the higher efficiency fiber filter and the first wet impinger or the final condenser system should be thoroughly rinsed with methylene chloride/methanol. This rinse shall be separated from the condensate. If the spent resin is transferred from the sorbent trap to a separate sample container for transport, the sorbent trap shall be thoroughly rinsed until all sample wetted surfaces appear clean. Visible films should be removed by brushing. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to this container.

Container No. 6. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3.

Impinger water. Treat the impingers as follows. Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight unless analysis of the impinger catch is required (see Organic Module).

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

Analysis. The analysis of samples obtained using this sampling system is a complex process and may utilize a wide variety of analytical procedures from this manual. Prior to sample collection with this system, a detailed test plan shall be developed and submitted to the Administrator for review. This test plan shall identify as a minimum, the process that is being tested, the pollutants that are expected to be present in the effluent streams, the analytical techniques that will be used to quantify pollutant emission levels and the anticipated detection limits of the techniques employed.

Probe nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 01.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

Pitot tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

Metering system. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump, for these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.0057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

L_d = Individual leakage rate observed during the leak-check conducted prior to the "i^{th}" component change (i = 1, 2, 3...n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5), °K (°R).

T_s = Absolute average stack gas temperature (see Figure 5), °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers and silica gel, ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 2), mm H_2O (in. H_2O).

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

Average dry gas meter temperature and average orifice pressure drop See Data sheeet (Figure 1.2.1.5).

Dry gas volume, correct the sample measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right) \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right] = K_1 V_m Y \ \frac{P_{bar} + (\Delta H/13.6)}{T_m} \qquad (1)$$

where:

K_1 = 0.3858° K/mm Hg for metric units.

= 17.64° R/in. Hg for English units.

Note: Equation 1 can be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceed L_p. If L_p or d exceeds L_a, Equation 1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 1 with the expression:

$V_m - (L_p - L_a)\ \theta$

Note: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

Probe heater calibration. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calilbration curves in APTD-0576 are used.

Temperature gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

Leak-check of metering system shown in Figure 1.2.1.8-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 1.2.1.8-5): close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

Barometer. Calibrate against a mercury barometer.

Calculations. Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

Nomenclature

A_n = Cross-sectional area of nozzle, $m^2(ft^2)$.

B_{ws} = Water vapor in the gas stream, proportion by volume.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.0057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

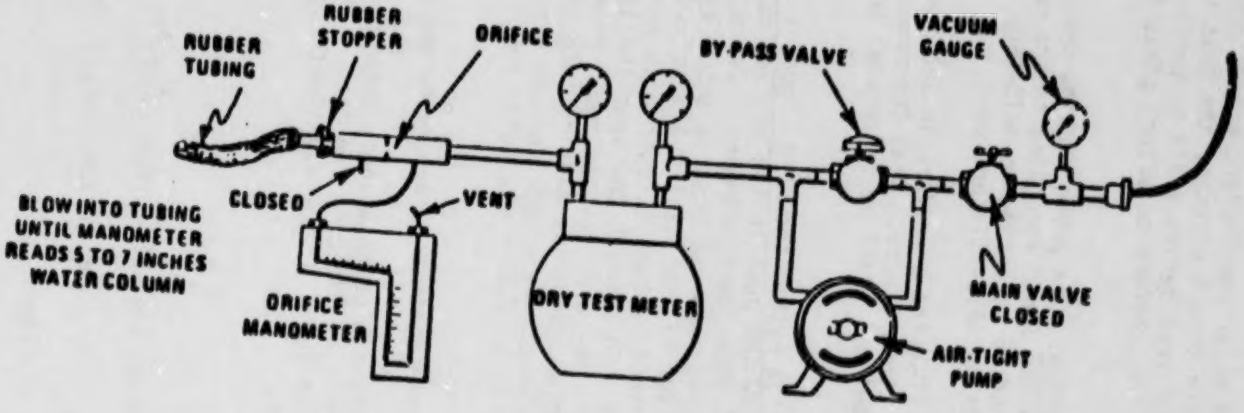
RUBBER TUBING
RUBBER STOPPER
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
BLOW INTO TUBING UNTIL MANOMETER READS 5 TO 7 INCHES WATER COLUMN
CLOSED
VENT
ORIFICE MANOMETER
DRY TEST METER
MAIN VALVE CLOSED
AIR-TIGHT PUMP

Figure 1.2.1.8 - 5. Leak Check of Meter Box.

(b) Case II. One or more component changes made during the samplng run. In this case, replace V_m in Equation 1 by the expression:

$$\left[V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_1 - (L_p - L_a)\theta_p \right]$$

and substitute only for those leakage rates (L_1 or L_p) which exceed L_a.

Volume of Water Vapor

$$V_{w(std)} = V_{1c}\left(\frac{P_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right) = K_w V_{1c} \qquad (2)$$

where

K_2 = 0.001333 m^3/ml for metric units.

= 0.04707 ft^3/ml for English units.

Moisture Content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad (3)$$

Note: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3), and a second from the assumption of saturated conditions. The lower of the two values B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 10 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1° C (2° F).

Conversion Factors

From	To	Multiply By
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

Isokinetic Variation

Calculation from Raw Data

$$I = \frac{100\, T_s[K_3 F_{1c} + (V_m/T_m)\,(P_{bar} + \Delta H/13.6)]}{600\, \theta V_s P_s A_n} \qquad (4)$$

where

K_3 = 0.003454 mm Hg-m^3/mL-°K for metric units

= 0.002669-in. Hg-ft^3/mL-°R for English units

Calculation for Intermediate Values

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s\ \theta A_n P_s 60(1-B_{ws})} \qquad (5)$$

$$= K_4\, \frac{T_s F_{m(std)}}{P_s V_s A_n \theta\ (1-B_{ws})}$$

where

K_4 = 4.320 for metric units

= 0.09450 for English units

Acceptable Results. If $90\% < I < 110\%$, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or if I is less than 90 percent, the Administrator may opt to accept the results.

To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

From prior analysis of the waste feed, concentration (POHCs) introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of OHC allowed to be present in the effluent. This may be expressed as:

$$\frac{(WF)\ (POHC_i\ conc)}{100}\ \frac{(100-\%DRE)}{100} = \text{Max } POHC_i \text{ Mass} \qquad (6)$$

where:

WF = mass flow rate of waste feed per hour (gm/hr) (lb/hr)

$POHC_i$ = Concentration of Principal Organic Hazardous Compound (wt%) introduced into the combustion process

DRE = Percent Destruction and Removal Efficiency required.

Max POHC = Mass flow rate (gm/hr) (lb/hr) of POHC emitted from the combustion source.

The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC to the volumetric flow rate being exhausted from the source. Volumetric flow rate data is available as a result of preliminary Method 1-4 determinations.

$$\frac{\text{Max } POHC_i \text{Mass}}{DV_{eff(std)}} = \text{Max } POHC_i \text{ conc} \qquad (7)$$

where:

$DV_{eff(std)}$ = Volumetric flow rate of exhaust gas in units of dry standard cubic meters or dry standard cubic feet.

$POHC_i$ conc = anticipated maximum concentration of the POHC in the exhaust gas stream (gm/dscm, lb/dscf).

In making this calculation, it is recommended that a safety margin of at least ten (10) be included:

$$\frac{LDL_{POHC} \times 10}{POHC_{iconc}} = V_{TBC} \qquad (8)$$

where

LDL_{POHC} = lower detection limit of POHC (gms or lbs)

V_{TBC} = minimum dry standard volume to be collected at dry gas meter.

1.2.1.8.1 References

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1.2.1.9 SOURCE ASSESSMENT SAMPLING SYSTEM (SASS) PROCEDURE

Procedure for Semi-quantitative Determination of Semivolatile Organic and Particulate Emissions from Stationary Sources

Principle and Applicability

Principle

Particulate and semi-volatile organic materials are withdrawn from a source at a constant rate near isokinetic conditions and are collected in a multi-component sampling train.

Three heated cyclones and a heated high-efficiency fiber filter remove and collect the particulate material from the sample and a packed bed of porous polymeric resin adsorbs the condensible organic vapors.

Chemical analyses of the sample are conducted to determine the concentration and identity of the semi-volatile organic species and gravimetric determinations are performed to approximate particulate emissions.

Applicability

This method is applicable to the preparation of semi-quantitative estimates (within a factor of three) of the amount and type of semi-volatile organic and particulate material that are discharged from incineration systems.

Apparatus

Sampling Train

A schematic of the sampling train used in this method is given in Figure 1.2.1.9-1. This sampling train configuration is that of the Source Assessment Sampling System (SASS) as supplied by the manufacturer. Basic operating and maintenance procedures are described in the "Operating and Service Manual: Source Assessment Sampling System" supplied with the purchase of the sampling system. Users should refer to this document and adopt, but not limit themselves to, these operating and maintenance procedures. The following subsections list the SASS train components and specifications as supplied.

Probe Nozzles

The probe nozzles are constructed of seamless stainless steel 316 tubing and have sharp, leading edges. The nozzles are a hybrid elbow/buttonhook design, obtainable in diameters ranging from 0.31 to 1.91 cm (1/8 to

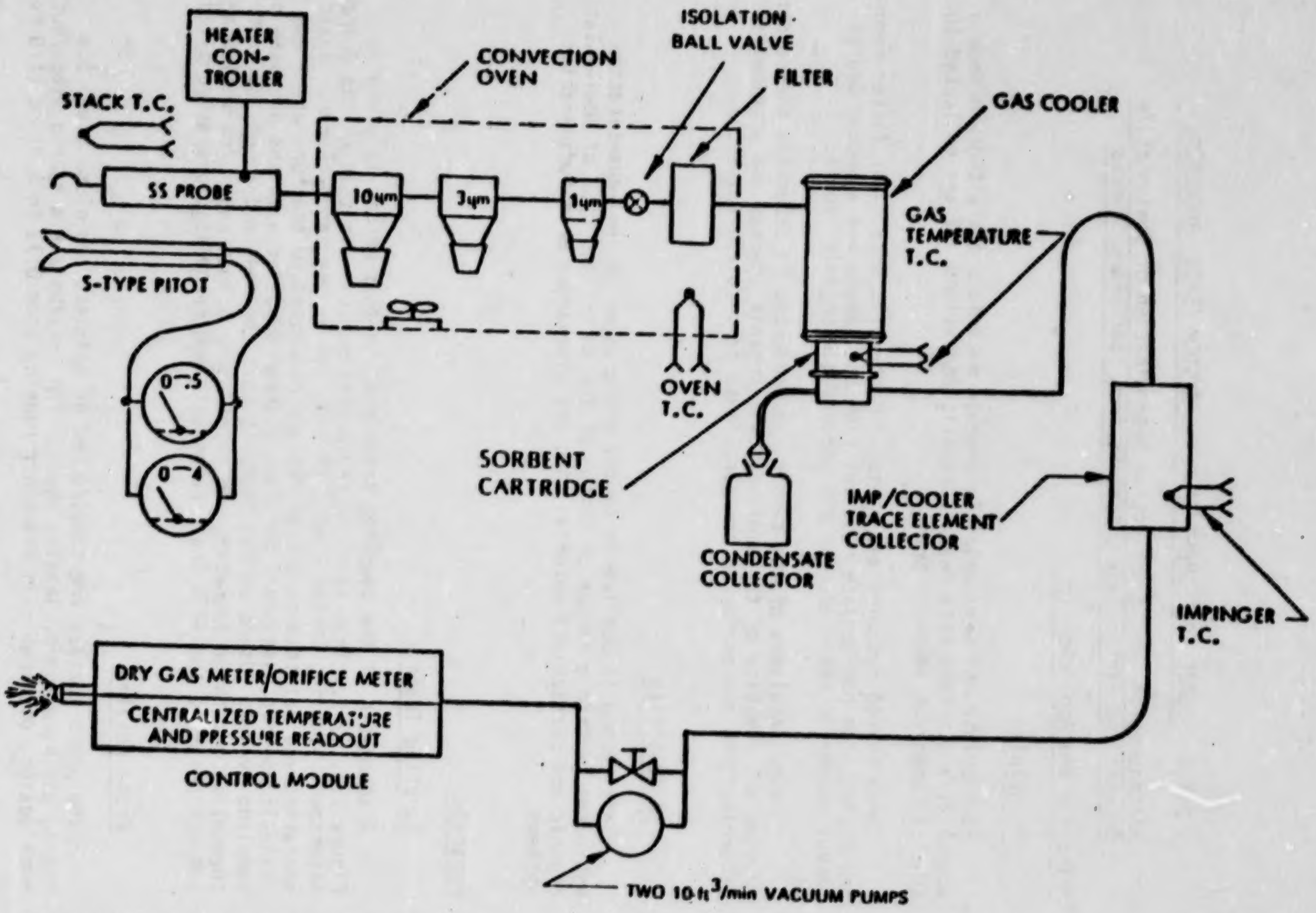
HEATER CON-TROLLER
STACK T.C.
SS PROBE
S-TYPE PITOT
0–.5
0–4
CONVECTION OVEN
10µm
3µm
1µm
ISOLATION BALL VALVE
FILTER
OVEN T.C.
GAS COOLER
GAS TEMPERATURE T.C.
SORBENT CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
TWO 10-ft³/min VACUUM PUMPS

Figure 1.2.1.9 - 1. SASS Schematic Diagram.
Source: IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201

3/4 inch), and are interchangeable. Each nozzle should be calibrated according to the procedure outlined in the Calibration section of this method.

Probe Liner

The probe liner is also constructed to Type 316 stainless steel seamless tubing; attached to the liner is a proportional temperature controller capable of maintaining the liner surface temperature at 204 + 20° C (400 + 36° F) during sampling. The use of the proportional controlTer to controT the liner surface temperature at the control module is preferred because the oven often cannot be reached for adjustment during sampling.

It should be noted that the measurement of the probe liner surface temperature is not an accurate measurement of the internal gas stream temperature, which is the temperature of interest. The temperature gradient that exists between the inner and outer walls of the liner is the reason for this source of error. Monitoring of the actual gas stream temperature is impractical with the SASS trains as presently constructed. It is suggested that a one-time calibration be conducted in which the internal gas stream temperature is compared to the liner surface at various temperatures and the standard SASS flow rate of 4.0 scfm.

The probe/probe liner can withstand temperatures up to 370° C (700° F) at which temperature they will soften. However, stack temperatures greater than 288° C (550° F) may result in gas temperatures at the 10-μm cyclone inlet greater than the recommended 204° C (400° F) and require the use of a special water- or forced-air-cooled probe.

Pitot Tubes

The pitot tubes are the Type "S", designed to meet the specifications of EPA Method (40 CFR 60); these are attached to the probe sheath to allow constant monitoring of the stack gas velocity. The point of attachment to the sheath is such that the impact (high pressure) opening plane of the pitots is level with or above the sampling nozzle entry plane, as required by Method 2 to eliminate nozzle interference in velocity measurements. If calibration is not required, the pitot tubes are assigned a nominal coefficient of 0.84, as described in the calibration section of this method.

Differential Pressure Gauges

Three of the Magnehelic® type gauges are used: one gauge (0 to 0.5 in. H_2O) for monitoring the pressure drop across the orifice meter (ΔH_i); the other two gauges (0 to 0.5 and 0 to 4.0 in. H_2O) are connected in parallel and indicate the pressure differential across the pitot tubes used for measuring stack gas velocity.

Filter Holder and Filter Support

The filter holder and filter support screen are constructed of Type 316 stainless steel with a Teflon® gasket providing an airtight seal around the circumference. The holder is attached immediately to the outlet of the 1-µm cyclone or the cyclone by-pass.

Cyclone/Filter Heating System

The cyclone/filter heating system is an insulated double-walled oven, capable of maintaining the temperature in the area of the cyclones and filter holder around the recommended 204 °C (400 °F). A chromel-alumel thermocouple for temperature sensing allows feedback control of the temperature to within approximately 10%.

Cyclone Train

The cyclone train consists of 3 cyclone separators in series, having nominal particle size cutoff diameters of 10-, 3- and 1-µm respectively. The material of construction is Type 316 stainless steel with Teflon® gaskets sealing the hoods and collector cups. The compact design of the 10-µm cyclone is achieved by incorporating flow-interrupting vanes in the collection cup.

Organic Module

the organic module consists of a thin-film heat exchanger/gas cooler, a sorbent cartridge and a condensate collection trap. The temperature of the heat exchanger fluid is regulated by activating an immersion heater or routing the coolant through another heat exchanger in the impinger ice water bath. Water from the impinger bath is continually circulated through the inner reservoir of the gas cooler for additional cooling capacity. The sorbent cartridge encloses the polymeric adsorbent bed in a cylinder covered on both ends by 80 mesh, Type 316 stainless steel wire cloth. The cartridge holds approximately 150 grams of XAD-2. Condensed moisture from the gas stream is collected in a reservoir located directly beneath the packed sorbent bed. The drain valve of the reservoir should be coupled with a Teflon® line to an appropriately-sized (1-5 liters) glass storage container, as the capacity of the reservoir will typically be exceeded during a run.

Impinger Train

The four impingers have a capacity of approximately 3 liters each and are constructed of pyrex glass. The caps are Teflon® with stainless steel fittings and the impingers are interconnected by flexible Teflon® or stainless steel tubing. The first two impingers are equipped with splash guards to minimize fluid carryover and the last impinger, with a thermocouple mounted in the cap for monitoring the impinger train exit gas temperature.

Pump/Metering System

Two leak-free vane-type vacuum pumps connected in parallel are used to maintain the 4.0 scfm flow in the sampling system. Vacuum and differential pressure gauges, thermocouples capable of measuring temperature to within 3°C (5.4°F) and a dry gas meter capable of measuring volume to within two percent are supplied as the other necessary components for maintaining isokinetic sampling rates.

Barometer

An aneroid or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.5 in Hg) is required, unless the barometric reading is obtained from a nearby national weather station; the station value (i.e., the absolute barometric pressure) must be corrected for elevation differences between the weather station and the sampling point. The corrected value should reflect a decrease of 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft.) elevation increase and vice versa for elevation decrease. The barometer must be calibrated against a mercury barometer as described in the calibration section of this method.

Gas Density Determination Apparatus

The length of a SASS run is typically sufficient to determine the average gas stream density during the run. EPA Method 3 should be consulted for detailed specifications of an integrated fixed gas sampling system. Analysis of the collected samples should be performed with an ORSAT analyzer or a GC/TCD system outfitted specifically for this purpose.

Calibration/Field Preparation Log

For documentation of calibration and preparation procedures, a permanently-bound laboratory notebook is recommended, in which carbon copies are made of the data as it is being recorded. The carbon copies should be detachable and only used for separate storage in the test program archives.

Sample Recovery Items

- Probe liner brush. The brush must have nylon bristles, a stainless steel wire handle and extensions of stainless steel, Teflon® or other inert material. The combined extensions must be equal to or greater than the length of the probe.
- Probe nozzle brush. The brush must have nylon bristles and a stainless steel wire handle, and be properly sized and shaped for cleaning the inner surfaces of the nozzle.

- Cyclone and filter holder brushes. The brushes must have nylon bristles and a stainless steel wire handle, and be properly sized for cleaning the inner walls of these components. It is strongly recommended that a separate brush be used for sample recovery from each of these components to avoid cross-contamination of one particle size fraction by another.

- Wash bottles. Three are needed; Teflon® or glass is required to avoid contamination of organic solvents; Teflon® is preferred because it is unbreakable.

- Glass sample storage containers. The containers must be chemically resistant, borosilicate glass bottles, 500-ml or 1,000-ml. Screw cap liners should either be Teflon® and/or constructed so as to be leak free and resistant to chemical attack by organic recovery solvents (narrow mouth glass bottles have been found to exhibit less tendency toward leakage).

- Petri dishes. These must be glass and sealed around the circumference with Teflon® tape for storage and transport of filter samples.

- Graduated cylinder and triple-beam balance. To measure condensed water to the nearest 1 ml or 0.5 gram. Graduated cylinders must have subdivisions no greater than 2 ml. The material of construction must be glass for measuring the volume of any solution that will be subject to organic analysis. Laboratory triple-beam balances are capable of weighing to ±0.5 gram or better.

- High-density linear polyethylene (HDLP) storage containers. These are used for storage of the impingers.

- Plastic storage containers. Air-tight containers are necessary for storage of silica gel.

- Funnels. To aid in recovery of samples for organic analysis, all glass funnels are required. Glass or plastic funnels may be used elsewhere but care must be taken to segregate the two types.

Reagents and Materials

The reagent descriptions and specifications used in sample collection and recovery are as follows:

Filters

Glass fiber filters 15.24 cm (6.0 in.), in diameter without organic binder, exhibiting 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles, conforming to the specifications outlined in ASTM standard Method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. The filter material must also be unreactive to SO_2 and SO_3.

Adsorbent Resin

Porous polymeric resin, XAD-2, is used. The resin must be cleaned prior to use. The resin must not exhibit a blank higher than 4 mg/kilogram of Total Chromatographable Organic (TCO) material prior to use. Once cleaned, the resin should be stored in a widemouth amber glass container and the headspace purged with nitrogen to limit exposure to ambient air. Resin should be used within two weeks of preparation.

Silica Gel

Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

Impinger Solutions

Since the impingers solutions are typically used for the determination of gas stream water-vapor content, distilled water should be used. If specific inorganic species are to be determined (e.g. hydrochloric acid when burning chlorinated organic material), then other appropriate collecting solutions (dilute base in the above example) must be used.

Crushed Ice

Commercially available. Quantities ranging from 50-100 lb may be necessary during a run, depending upon ambient air temperatures.

Methanol/Methylene Chloride

Distilled-in-glass or pesticide-grade methanol and methylene chloride are required as a minimum.

Sampling

Sampling Equipment Calibration

The probe tips, pitot tubes, dry gas meter, thermocouples and any thermometers must be calibrated before and after each field sampling trip according to the procedures outlined in APTD-0576. During extended sampling trips where the train will routinely be used more than 10 times, it is strongly recommended that a calibrated orifice, a set of micrometers (Vernier calipers) and a standard mercury-in-glass thermometer accompany the train to verify that the calibration of the dry gas meter, probe nozzles and thermocouples respectively, have not changed significantly (greater than ±2%). The aneroid barometer should be calibrated on a daily basis against a mercury barometer when in the laboratory and periodically in the field by consulting the local weather station and correcting for elevation.

Laboratory Preparation

Weigh several 700-800-g portions of silica gel in air-tight containers to ±0.1 g. Record the weight of the silica gel plus the container on the container and in a field sampling preparation notebook.

Holding with blunt-tipped tweezers, check filters visually against light for irregularities, flaws or pinhole leaks. Label the shipping containers (glass petri dishes) and keep the filters in these containers at all times except during sampling and weighing. The filters themselves need not be labelled if strict compliance with the above instruction is insured. Desiccate the filters in a desiccator over Drierite® or silica gel with the petri dishes open at 20 ±5.6°C (68 ±10°F) and ambient pressure for at least 24 hours and weigh. Thereafter weight at intervals of a minimum of 6 hours to a constant weight, i.e., previous weight ±0.5 mg; record the weight to the nearest 0.1 mg, along with the date and time in the field sampling preparation notebook. Alternatively, the filters may be oven-dried at 105°C (220°F) for 2 to 3 hours, desiccated for 2 hours, weighed, and weighed thereafter at intervals of 6 hours to a constant weight. During each weighing, the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity greater than 50 percent.

Passivate all SASS train parts and sample storage containers, referring to the procedure that appears in Appendix C, adapted from Level 1 requirements. Passivation is required of all new train components and sample storage containers before their initial use in the field. Thereafter, passivation should be conducted every 6 months when the frequency of tests is once per month or less, and every 3 months when the frequency is between once per week and once per month. If testing is more frequent, passivation should be conducted proportionately more often. Whenever corrosion has occurred, the corrosion must be removed and the passivation repeated. The passivation and rinse solutions should be replaced every fourth use, or discarded weekly.

Prepare recycled sample containers by detergent washing (using a stiff nylon brush where necessary), followed by rinsing with distilled-deionized water, methanol and methylene chloride. As each part is treated with the final solvent, dry with filtered air or dry nitrogen and inspect for any contaminating residue. Discard any container exhibiting visual contamination. Cover all open surfaces with aluminum foil or Teflon® film, using elastic bands to secure.

Assembly and leak-checking of the entire train in the laboratory is highly recommended to reveal the need for replacement of gaskets or defective components. The leak check procedure is described in this procedure. Substitution of Viton-A gaskets for Teflon® may facilitate meeting the allowable leak rate. A length of Teflon® tape stretched around the circumference of each flanged connection underneath the ring clamp also greatly reduces inward air leakage.

Preliminary Field Determinations

Select the sampling site and remove any accumulated scale and corrosion from the sampling portholes. Determine the stack static pressure, temperature and velocity profile using EPA Method 2; a leak check of the pitot lines prior to conducting these measurements is highly recommended. Approximate the moisture content using EPA Method 4 (Approximation Method) or alternate means such as drying tubes, wet bulb/dry bulb or condensation techniques, stoichiometric calculations or previous experience. Determine the stack gas dry molecular weight by performing an ORSAT or GC/TCD analysis for CO, CO_2, O_2 and N_2 on an average of three grab samples taken from either the center of the duct or a point no closer to the stack walls than 1.0 m (3.3 ft).

Select a nozzle size based upon the calculations below, ensuring that it will not be necessary to change the nozzle during the sampling run to maintain near-isokinetic sampling rates.

Calculation of the Required Nozzle Diameter

(1) First calculate the Average Stack Gas Velocity:

$$(V_s)_{avg} = K_p C_p \left(\sqrt{(\Delta P)} \right)_{avg} \left[\sqrt{\frac{(T_s)_{avg}}{P_s M_s}} \right]$$

where:

$(V_s)_{avg}$ = Average stack gas velocity, ft/sec

K_p = $85.48 \left(\frac{ft}{sec} \left[\frac{(lb/lb\text{-}mole)(in.\ H_2O)}{°R(in.\ H_2O)} \right]^{1/2} \right)$

C_p = Pitot tube coefficient, dimensionless

ΔP = Velocity head of stack gas, in. H_2O

$(T_s)_{avg}$ = Average stack gas temperature, °R

P_s = Absolute stack gas pressure, in. Hg

M_s = Molecular weight of stack gas (wet basis), lb/lb-mole

(2) Then calculate the required Nozzle Diameter:

$$D_n = 0.831 \quad \frac{(T_s)_{avg}}{(V_s)_{avg} P_s}$$

Select a suitable probe length such that one or more points of average velocity can be sampled. Determine the total length of sampling time by comparing the anticipated average sampling rate to the volume requirement of 30 dscm (approximately 1060 dscf).

The anticipated Average Sampling Rate is calculated as follows:

$$Q_{mo} = (1-B_{ws})Q_{st} \frac{P_{st}\,[(T_m)_{avg}]}{P_m\,(T_{st})}$$

where:

Q_{mo} = Flow rate through orifice at meter conditions, ft^3/min (dry)

B_{ws} = Volume fraction of water vapor in the gas stream, dimensionless

Q_{st} = Design sampling flowrate for SASS train, 4.0 scfm

P_{st} = Standard presssure, 29.92 in. Hg

$(T_m)_{avg}$ = (estimated) Average gas temperature at the dry gas meter, °R

P_m = Absolute meter pressure, in. Hg[1]

T_{st} = Standard temperature, 528 °R

Using this result, obtain the approximate sampling time by dividing the required sample volume by the estimated sampling flowrate.

Finally, calculate the Orifice Pressure Drop needed to maintain near-isokinetic sampling conditions from the equation:

$$\Delta H_i = \frac{P_m}{(T_m)_{avg}} \left[\frac{0.1924\, Q_{mo}}{J_i D_{oi}^2}\right]^2$$

---

[1] $$P_m = P_b + \frac{(\Delta H)_{est.avg.}}{13.6}$$

where:

P_m = Absolute meter pressure, in. Hg

$(\Delta H)_{est.avg.}$ = Estimated average ΔH across orifice, 0-0.5 in. H_2O

P_b = Barometric pressure (corrected), in. Hg

where:

ΔH_i = Required ΔH across the orifice, in. H_2O

P_m = Absolute meter pressure, in. Hg[1]

$(T_m)_{avg}$ = (estimated) Average gas temperature at the dry gas meter, °F

J_i = Orifice coefficient for orifice "i"[2]

D_{oi} = Orifice diameter, inches[3]

It is desirable, but not required, to sample more than one point of average velocity during a SASS run. Allocate equal intervals of the total sampling time estimated above to each sampling point chosen if more than one point will be sampled.

Preparation of the Collection Train

An integral part of preparing the collection train is securing sufficient electrical power to operate for an extended period of time without interruption. Three separate circuits - two thirty-ampere (30 amp) and one twenty-ampere (20 amp) - are required. It is highly recommended that one sampling pump and one control box power cord (probe heater) be placed on one of the 30-amp circuits, and the other sampling pump and control box power cord (oven heater and temperature readout) be placed on the other 30-amp circuit. The organic module coolant pump and temperature controller should be placed on the smaller 20-amp circuit.

During assembly of the train, keep the inner surfaces of each component covered until it is integrated into the system and sampling is about to begin. Fill the sorbent trap section of the organic module[4] with approximately 150 g of clean adsorbent resin. Pack the trap uniformly to eliminate potential channeling. Place 500 ml of distilled water or other appropriate solution[5] into the first and second impingers, leave the third impinger empty and place a preweighed portion of silica gel into the fourth. Using blunt-tipped tweezers, place a tared filter into the filter holder. Insure that the filter is centered and the gasket properly placed to prevent the gas stream from circumventing the filter. On the probe, mark the locations of the chosen sampling points with heat-resistant tape or paint.

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[1] Refer to note 1 on previous page.

[2] See "Operating and Service Manual" and the Calibration Section of this Method for determining orifice coefficients.

[3] Information supplied upon purchase of the SASS train; the largest diameter orifice is typically best suited for the SASS sampling rate of 4.0 scfm.

[4] To avoid contamination, the trap should be placed upon a clean surface (i.e. aluminum foil rinsed with methylene chloride and air-dried) while filling and gloves should be worn.

[5] The choice of impinger solutions depends upon whether these will be used to collect selected inorganic species or to simply condense water vapor from the gas stream to measure percent moisutre. For example, in an incinerator combusting chlorinated organic material, a solution of dilute base would typically be used to collect hydrochloride acid emissions.

The stepwise procedure for assembly of the train follows:

1. Place the oven on a table or rollers that will be used as a support throughout the run.
2. Assemble the three cylcones,[1] using the vortex breaker supplied with the cyclone in the 10-μm cyclone only. Do not use the vortex breakers supplied with the 3- and 1-μm cyclones in the 3- and 1-μm cyclones, respectively.[2]
3. Attach the filter holder to the outlet of the 1-μm cyclone and place the cyclones and filter holder together in the oven. Preheat a spare filter holder containing a tared filter on the oven floor; cover the holder openings with aluminum foil.
4. Attach the probe to the oven and to the 10-μm cyclone.
5. Place the impingers in the tray in the impinger case and make the appropriate interconnections.
6. Connect the organic module inlet to the filter housing outlet and the organic module outlet to the first impinger inlet.
7. Connect the vacuum pumps in parallel to the fourth impinger outlet.
8. Connect all temperature sensors and power lines to the control unit. Check temperature indicators and controllers at ambient temperature.
9. Activate gas cooling system. Begin monitoring the XAD-2 temperature. Always check coolant level before supplying power. Insure proper gas cooling system temperature before proceeding.

   IT IS EXTREMELY IMPORTANT THAT THE XAD-2 RESIN TEMPERATURE NEVER EXCEED 50°C, AS DECOMPOSITION WILL OCCUR. DURING TESTING, THE XAD-2 TEMPERATURE MUST NOT EXCEED 20°C FOR EFFICIENT CAPTURE OF THE SEMIVOLATILE ORGANIC SPECIES OF INTEREST.
10. Heat oven and probe to 204°C (400°F).
11. Run gas flow leak check.

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[1] To minimize leaks throughout the system, it is suggested that a strip of Teflon® tape be stretched around the circumference of each flanged seal and the ring clamp placed over and secured.

[2] Actual calibration data has shown that the use of the vortex breakers in the two smaller cyclones may result in unreproducible particle size cut-off diameters, i.e., the particle size at which 50% collection efficiency is exhibited.

The following instructions will facilitate the leak-checking procedure:

- Open the isolation ball valve and plug the inlet to the probe with a rubber stopper or appropriate air-tight cap.

- Start the pumping system with the bypass valves fully open and the coarse valves completely closed. Partially open the coarse valves and slowly close the bypass valves until a vacuum of 127 mm Hg (5 in. Hg) is reached. Do not reverse the direction of the bypass valves as backflushing of the impinger solutions into the organic module will result. If the desired vacuum is exceeded, either leak check at the higher vacuum or terminate the leak check and begin again. Allow the system to equilibrate and measure the leakage rate. The allowable leak rate for the SASS train is 0.0014 m^3/min (0.05 ft^3/min) at this vacuum. Close the isolation ball valve and evacuate the train to 281 mm Hg (15 in. Hg). The leak rate through the back half of the train should be less than 0.0014 m^3/min (0.05 ft^3/min) at this vacuum.

- When the leak-check is complete, slowly remove the plug from the probe tip and then slowly open the isolation ball valve.

- When the vacuum drops to 5 in. Hg or less, immediately close both coarse control valves together. Switch off the pumping system and reopen the bypass valves. The bypass valves should not be opened until the coarse valves have been closed.

  Post-test leak checks only are mandatory; however, experience has shown that pre-test leak checks and leak checks following component changes are necessary to insure that invaluable sampling time is not lost as a result of an oversight or defective component.

Sample Collection

Constant monitoring of train operations before, during and after the particulate run are essential in maintaining sample integrity. Listed below are sample collection guidelines:

1. With the coarse valves closed and bypass valves open, turn on the vacuum pumps and allow them to warm up. As the probe and oven are heating, prepare a SASS run data sheet as shown in 40 CFR Appendix A. Barometric pressure data should be recorded at the beginning and end of the run at a minimum; once per hour is preferred.

2. When operating temperatures have been reached, place the probe in the stack at the first designated sampling point, turn on the vacuum pumps, adjust the sampling flowrate to achieve the calculated ΔH_i, and start the elapsed timer. If, however, the gas stream is under a medium or high negative pressure, it becomes extremely important to start the vacuum pumps just before placing the probe in the gas

stream, and to continue to operate the pumps until just after the probe has been removed from the gas stream. This will eliminate the possibility of lifting of the filter or backflushing of the filter and cyclone particulate catches at any time.

3. Seal the sampling port around the probe to prevent introduction of dilution air at this point. Record the clock time of the start of the test.

4. Using the criterion outlined under Preliminary Field Determination, place the integrated fixed gas bag or bulb sampling probe into the gas stream and begin sampling. Collect 3 samples during the SASS run; record the initial and final clock times of each integrated fixed gas sample.

5. Monitor and maintain all temperatures and the calculated ΔH and record the data at equal intervals of 10-15 minutes.

6. Add crushed ice to the impinger section and drain excess water as necessary.

7. Without interrupting sampling, drain the condensate initially, every 30-45 minutes, and afterward, as necessary. Insure that the vessel into which the reservoir is drained forms an airtight system with the reservoir using a connecting Teflon® line, and is placed well below the level of the reservoir itself. To drain the reservoir, close the isolation ball valve and open the drain valve. Allow the system to evacuate for 10-20 secs. Carefully open the isolation valve. The condensate should siphon from the reservoir into the storage vessel. Close the drain valve when the siphoning action of the condensate ceases.

8. Replace the filter when it becomes impossible to maintain near-isokinetic sampling rates but not more frequently than every 20-30 min. Always terminate and initiate sampling by adjustment of the coarse pump valves and then the bypass valves. A spare filter holder and filter, if available, should be preheating in the oven at all times. Conduct leak checks before and after changing the filter. Recall previous instructions concerning removal and re-introduction of the probe into the duct.

9. At the same time, check the 1-μm cyclone reservoir for remaining capacity, taking care not to contaminate the contents during this inspection.

10. When replacing a filter, start and stop the fixed gas sampling concurrently with the SASS sampling; record the clock time and dry gas meter reading whenever sampling is interrupted.

11. Upon collection of the required 30 dscm (1060 dscf), remove the probe from the gas stream and shut down the pumps as previously instructed. Record the final dry gas meter reading and clock time; turn off all heaters. Conduct the post-test leak check when the probe tip can be safely handled. Do not cap the probe while initially cooling, because this will create a vacuum inside that will cause disruption of the cyclone and filter particulate catches when it is released. Instead, use aluminum foil to cover probe openings.[1] Leak check the pitot lines per EPA Method 2 to validate velocity heat data.

Sample Recovery

Disassembly of the SASS Train

At the conclusion of the sampling run, the train is disassembled and transported to the prepared work area as follows:

1. Leaving the fan operating, open the cyclone oven door to expedite cooling. When the probe can be safety handled, disconnect from the 10-μm cyclone inlet. Wipe off external particulate matter near the probe tip and place a cap over each end. The probe must remain level throughout this procedure.

   Care must be taken to avoid tightly capping train components as they are cooling from stack or oven temperatures. This will eliminate the possibility of creating a vacuum inside which, when released, may disrupt and backflush the cyclone and filter particulate catches into one another.

2. Disconnect the line joining the filter outlet to XAD-2 module and cap off:

   a. The 10-μm cyclone inlet.

   b. The filter holder outlet.

   c. The inlet of the line just disconnected from the filter holder outlet.

   Disconnect the filter holder and cap the inlet. Set aside with the inlet facing upward. Cap the outlet of the 1-μm cyclone. The cyclones must remain upright throughout this procedure. The cyclones can now be disconnected from one another or moved to the recovery area as a single unit.

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[1] Before the probe is transported, secure the aluminum foil covers with elastic bands.

3. Disconnect the line joining the XAD-2 module to the impinger system at the organic module outlet. Cap the organic module outlet.

4. Disconnect the silica gel impinger outlet from the vacuum line to the pumps; cap off the first impinger inlet and the fourth impinger outlet.

Sample Handling and Transfer

The sample handling and transfer prodedures outlined in this section have been adopted from the Level 1 procedures. The flow diagrammatic representation of the sample recovery procedures shown in Figures 1.2.1.9-2, -3, and -4 can be found in the Level 1 Sampling and Analysis Procedures Manual.

Nozzle, Probe, Cyclones, and Filter

The step-by-step procedures for the recovery of particulate material collected in the nozzle, probe, and cyclones, and on the filter are detailed below:

1. Carefully transfer the filter from the filter housing to its original glass petri dish; a pair of clean blunt-tipped tweezers and a flat spatula should be used for handling the filter. Using a clean nylon-bristled brush, add any particulate material from the front half of the filter housing to the petri dish; seal the petri dish around the circumference with 1-in. wide Teflon tape; store with the collected particulate material facing upward.

2. Tap and brush any particulate material adhering to the walls of the upper chamber of the 1-μm cyclone into the lower cup; remove the cup and quantitatively transfer the bulk contents to a wide-mouth amber glass jar. Rinse the brush with methanol/methylene chloride (50:50) into the probe rinse container.

3. Recover the contents of the 3-μm cyclone in the same manner using a separate wide-mouth amber glass jar.

4. Recover the contents of the 10-μm cyclone in the same manner using a separate wide-mouth amber glass jar.

5. Reconnect the lower cups of each cyclone and rinse any particulate material adhering to the walls (until the walls appear clean) down into the cups with the methanol/methylene chloride mixture. Remove the lower cups and transfer the contents to the probe rinse container. Rinse the interconnecting tubing among the cyclones into the probe rinse in the same manner.

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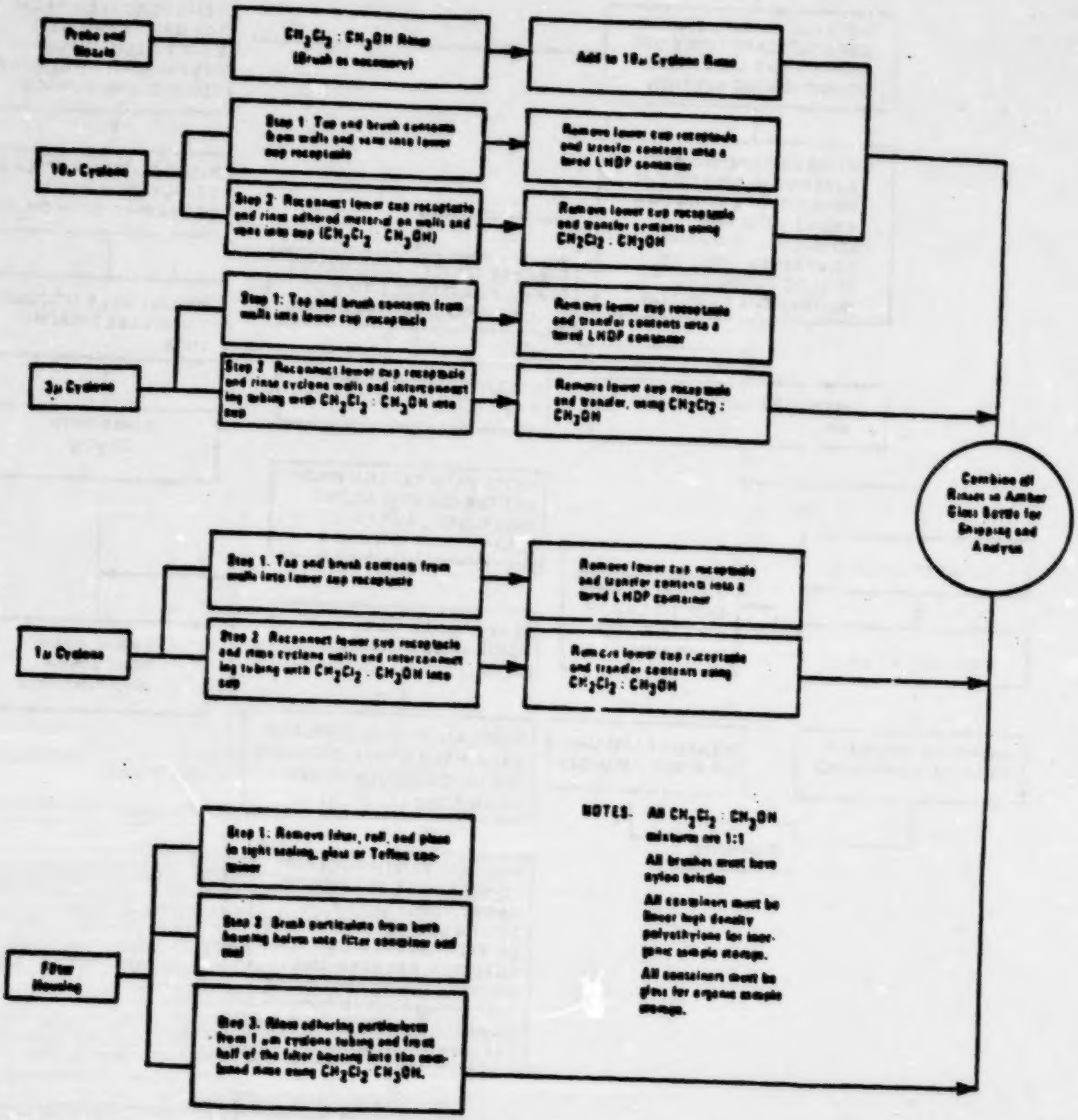
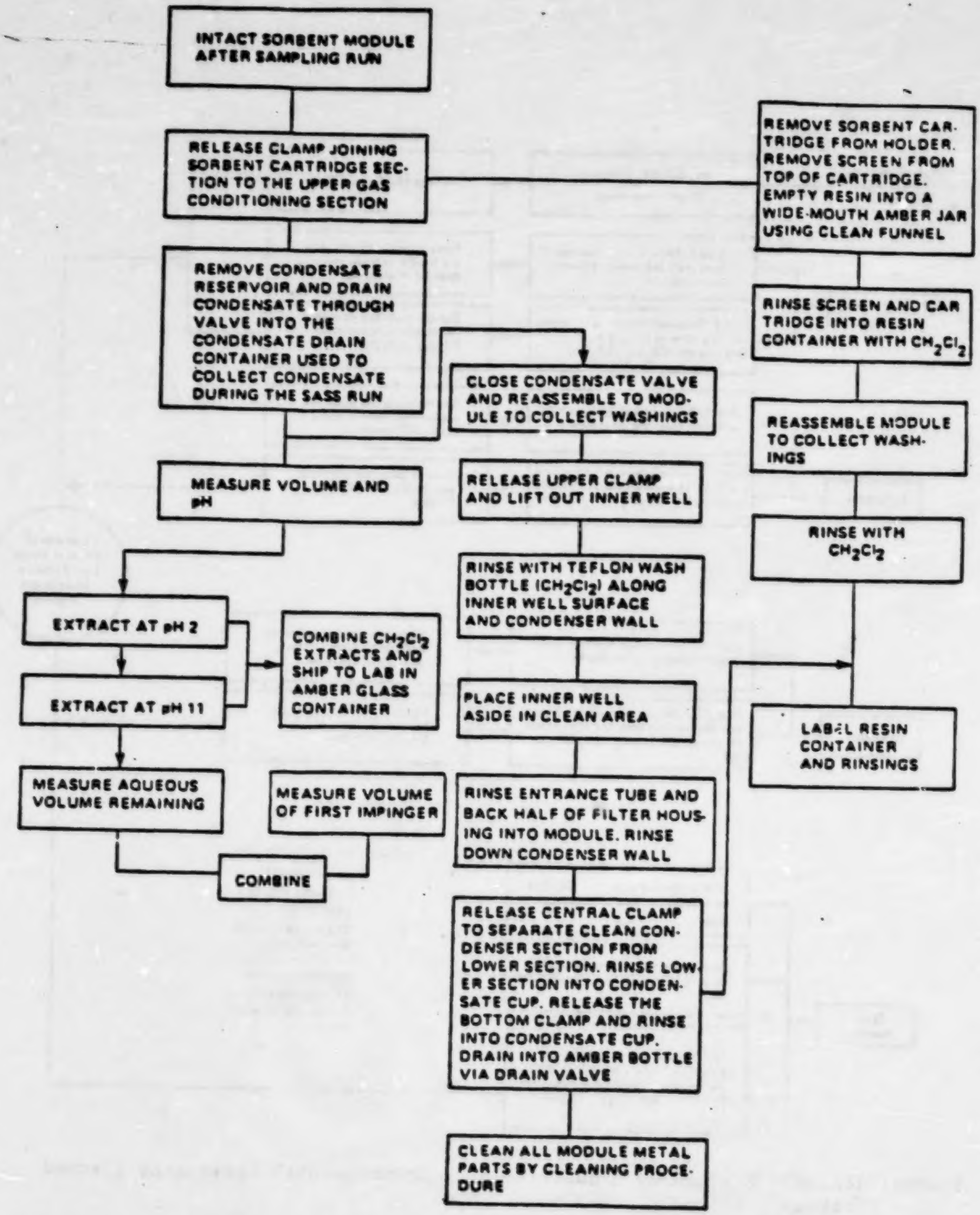

Probe and Nozzle
CH₂Cl₂ : CH₃OH Rinse (Brush as necessary)
Add to 10μ Cyclone Rinse
10μ Cyclone
Step 1: Tap and brush contents from walls and vane into lower cup receptacle
Remove lower cup receptacle and transfer contents into a tared LHDP container
Step 2: Reconnect lower cup receptacle and rinse adhered material on walls and vane into cup (CH₂Cl₂ : CH₃OH)
Remove lower cup receptacle and transfer contents using CH₂Cl₂ : CH₃OH
3μ Cyclone
Step 1: Tap and brush contents from walls into lower cup receptacle
Remove lower cup receptacle and transfer contents into a tared LHDP container
Step 2: Reconnect lower cup receptacle and rinse cyclone walls and interconnecting tubing with CH₂Cl₂ : CH₃OH into cup
Remove lower cup receptacle and transfer, using CH₂Cl₂ : CH₃OH
Combine all Rinses in Amber Glass Bottle for Shipping and Analysis
1μ Cyclone
Step 1. Tap and brush contents from walls into lower cup receptacle
Remove lower cup receptacle and transfer contents into a tared LHDP container
Step 2. Reconnect lower cup receptacle and rinse cyclone walls and interconnecting tubing with CH₂Cl₂ : CH₃OH into cup
Remove lower cup receptacle and transfer contents using CH₂Cl₂ : CH₃OH
Filter Housing
Step 1: Remove filter, roll, and place in tight sealing, glass or Teflon container
Step 2. Brush particulate from both housing halves into filter container and seal
Step 3. Rinse adhering particulates from 1 μm cyclone tubing and front half of the filter housing into the combined rinse using CH₂Cl₂ : CH₃OH.
NOTES. All CH₂Cl₂ : CH₃OH mixtures are 1:1
All brushes must have nylon bristles
All containers must be linear high density polyethylene for inorganic sample storage.
All containers must be glass for organic sample storage.

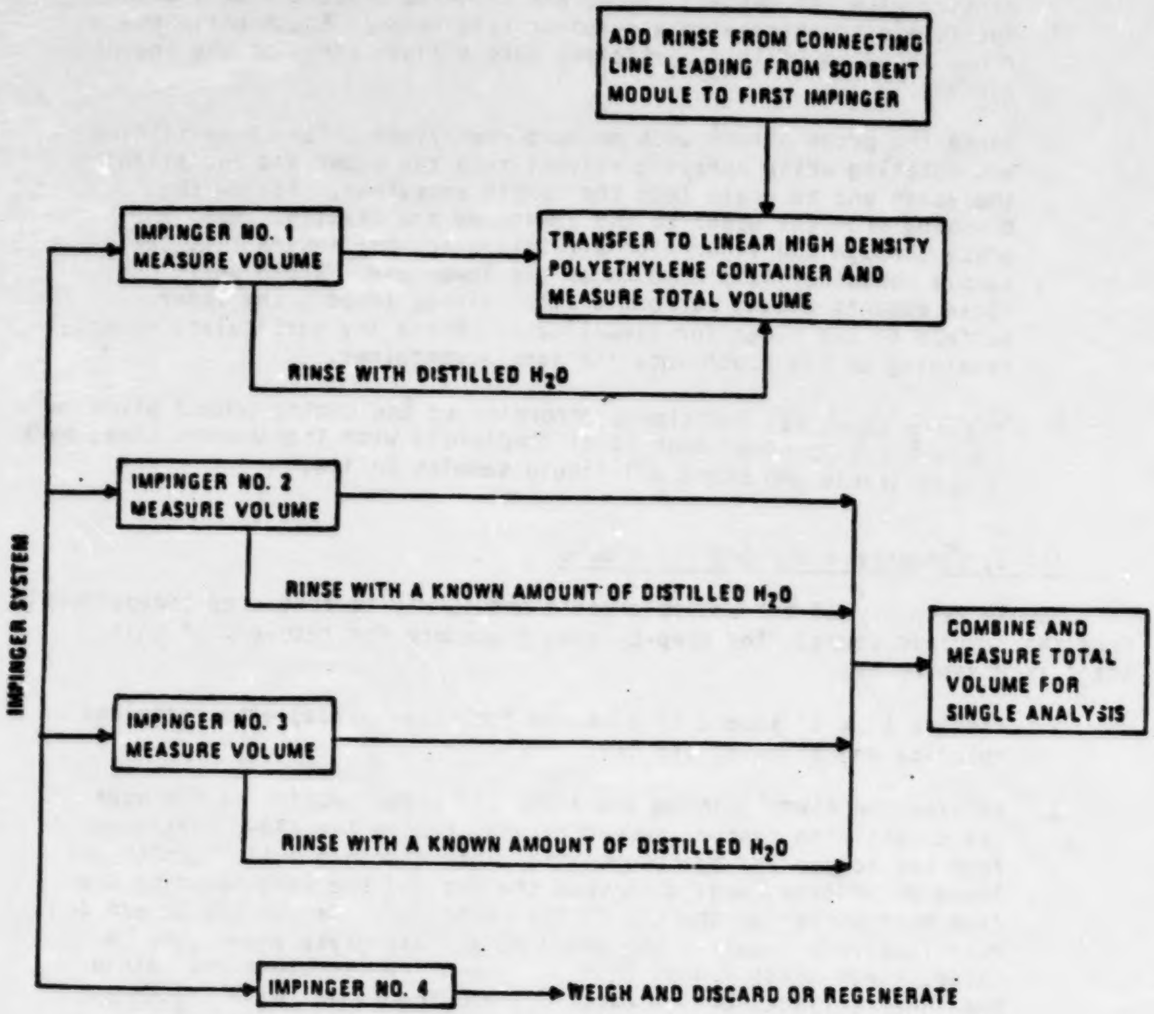
Source: "IERL-RTP Procedures Manual: Level I Environmental Assessment (Second Edition)", EPA-600/7-78-201

Figure 1.2.1.9 - 2. Sample Handling and Transfer Nozzle, Probe, Cyclones and Filter.


INTACT SORBENT MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING SORBENT CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE CONDENSATE RESERVOIR AND DRAIN CONDENSATE THROUGH VALVE INTO THE CONDENSATE DRAIN CONTAINER USED TO COLLECT CONDENSATE DURING THE SASS RUN
MEASURE VOLUME AND pH
EXTRACT AT pH 2
EXTRACT AT pH 11
COMBINE CH_2Cl_2 EXTRACTS AND SHIP TO LAB IN AMBER GLASS CONTAINER
MEASURE AQUEOUS VOLUME REMAINING
MEASURE VOLUME OF FIRST IMPINGER
COMBINE
CLOSE CONDENSATE VALVE AND REASSEMBLE TO MODULE TO COLLECT WASHINGS
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
RINSE WITH TEFLON WASH BOTTLE (CH_2Cl_2) ALONG INNER WELL SURFACE AND CONDENSER WALL
PLACE INNER WELL ASIDE IN CLEAN AREA
RINSE ENTRANCE TUBE AND BACK HALF OF FILTER HOUSING INTO MODULE. RINSE DOWN CONDENSER WALL
RELEASE CENTRAL CLAMP TO SEPARATE CLEAN CONDENSER SECTION FROM LOWER SECTION. RINSE LOWER SECTION INTO CONDENSATE CUP. RELEASE THE BOTTOM CLAMP AND RINSE INTO CONDENSATE CUP. DRAIN INTO AMBER BOTTLE VIA DRAIN VALVE
CLEAN ALL MODULE METAL PARTS BY CLEANING PROCEDURE
REMOVE SORBENT CARTRIDGE FROM HOLDER. REMOVE SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO A WIDE-MOUTH AMBER JAR USING CLEAN FUNNEL
RINSE SCREEN AND CARTRIDGE INTO RESIN CONTAINER WITH CH_2Cl_2
REASSEMBLE MODULE TO COLLECT WASHINGS
RINSE WITH CH_2Cl_2
LABEL RESIN CONTAINER AND RINSINGS

Source: "IERL-RTP Procedures Manual: Level I Environmental Assessment (Second Edition)", EPA-600/7-78-201.

Figure 1.2.1.9 - 3. Sample Handling and Transfer -- XAD - 2 Module.


ADD RINSE FROM CONNECTING LINE LEADING FROM SORBENT MODULE TO FIRST IMPINGER
IMPINGER NO. 1 MEASURE VOLUME
TRANSFER TO LINEAR HIGH DENSITY POLYETHYLENE CONTAINER AND MEASURE TOTAL VOLUME
RINSE WITH DISTILLED H_2O
IMPINGER SYSTEM
IMPINGER NO. 2 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DISTILLED H_2O
COMBINE AND MEASURE TOTAL VOLUME FOR SINGLE ANALYSIS
IMPINGER NO. 3 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DISTILLED H_2O
IMPINGER NO. 4
WEIGH AND DISCARD OR REGENERATE

Source: "IERL-RTP Procedures Manual: Level I Environmental Assessment (Second Edition)", EPA-600/7-78-201.

Figure 1.2.1.9 - 4. Sample Handling and Transfer Impingers.

6. Carefully remove the probe nozzle and clean the inside surface by rinsing with the methanol/methylene chloride mixture from a wash bottle and brushing with a nylon-bristle brush. Brush until the rinse shows no visible particles; make a final rinse of the inside surface.

   Rinse the probe liner[1] with methanol/methylene chloride by tilting and rotating while spraying solvent into the upper end and allowing the lower end to drain into the sample container. Follow the brushing from the upper to the lower end and rinsing. Push the brush through the liner with a twisting action; insure that the sample container is placed under the lower end. Brush until the rinse appears clean; perform a final rinse. Inspect the inner surface of the liner for cleanliness. Rinse any particulate material remaining on the brush into the sample container.

7. Clearly label all containers according to the coding scheme given in Table 1.2.1.9; cover each label completely with transparent tape; mark liquid levels and store all liquid samples on ice.

XAD-2, Condensate and Organic Module

Sample recovery of the entire organic module may be conducted independently from the previous steps. The step-by-step procedure for recovery of this stage is given below.

1. Rinse a 1' x 1' square of aluminum foil (dull side) with methylene chloride and allow to air dry.

2. Release the clamp joining the XAD-2 cartridge section to the upper gas conditining system (second clamp), remove the XAD-2 cartridge from the holder and place upon the clean aluminum foil. GENTLY pry loose or unscrew (depending upon the design) the ring securing the fine mesh screen on the top of the cartridge. Remove the screen and quantitatively transfer the XAD-2 to a clean glass amber jar. A large, clean glass funnel should be used for the transfer. Rinse the inner surfaces of the cartridge and the funnel with CH_2CL_2 as necessary to remove adhering XAD-2. Any XAD-2 that escapes onto the aluminum foil should be retrieved and added to the sample.

3. Replace the screen on the cartridge, reinsert the cartridge into the module and reassemble the module. One person can accomplish this task by butting the lower section in its proper sealing position up against the upper section while securing the ring clamp. One or more wooden spacers approximately 1/2-in. thick are suggested for this purpose.

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[1] It is suggested that two people perform this task to minimize the possibility of accidental sample loss.

TABLE 1.2.1.9. Suggested format for sample coding and identification

Sample code	Container	Size	Sample description
1C	Amber glass	100 ml, wide-mouth	1-μm cyclone catch
3C	Amber glass	100 ml, wide-mouth	3-μm cyclone catch
10C	Amber glass	100 ml, wide-mouth	10-μm cyclone catch
PF-a,b,c,...	Glass petri dish	>6-in. diam.	Particulate filter(s)
PR	Amber glass	1 liter	Methylene chloride/methanol front-half rinse
PRB	Amber glass	500 ml	Methylene chloride/methanol blank
MRX	Amber glass	1 liter	Methylene chloride back half rinse
MRXB	Amber glass	500 ml	XAD-2 resin blank
CD-LE	Amber glass	1 liter	Methylene chloride condensate extract
CD-LEB	Amber glass	500 ml	Methylene chloride blank
AR-I1	HDLP[a]	1 liter	Aqueous residue of condensate combined with first impinger catch
I1B	HDLP	500 ml	First impinger blank (distilled H_2O or other appropriate solution)
I23	HDLP	1 liter	Second and third impinger catches
I23B	HDLP	500 ml	Second and third impinger blank (distilled H_2O or other appropriate solution)

[a] HDLP = High Density Linear Polyethylene.

4. Open the condensate reservoir valve and drain the remaining condensate into the condensate storage container. Measure and record the volume and pH (using narrow-range pH paper) of the entire condensate.

5. Transfer the entire condensate to an appropriately-sized separatory funnel. Adjust the pH of the condensate (as indicated by the narrow-range pH paper) to 1-2 using (ultrapure or reagent grade) nitric acid. Extract the condensate three times with methylene chloride, each time with fresh portions measuring 8-10% of the total condensate volume. If the volume of the condensate is extremely large (¨1800 ml), the condensate may be extracted in portions, but fresh volumes of methylene chloride must be used for each and every extraction. After each addition of methylene chloride to the separatory funnel, the funnel must be shaken with periodic venting through the stopcock[1] to relieve any vapor pressure. When no further vapor pressure can be vented after shaking, the funnel should be mounted upright on a ring stand, the cap removed, the layers allowed to separate and the methylene chloride (bottom) layer removed. If an emulsion forms equal to more than 1/3 the size of the solvent layer, reagent-grade sodium chloride should be added until the emulsion is broken or reduced to meet the above criterion. The emulsion interface should not be included as part of the methylene chloride extract.

6. Following the third extraction of the acidified condensate, adjust the pH of the aqueous residue to 11-12 with a 50% w/w solution of sodium hydroxide (as indicated by narrow-range pH paper), extract with methylene chloride in the same manner, and combine the methylene chloride extracts of the condensate at the high and low pH's.

7. Transfer the aqueous residue from this extraction to a clean nalgene container; retain for later addition of the first impinger solution.

8. Insure that the condensate reservoir valve is closed, release the upper clamp and lift the inner well halfway out of the module. Rinse the inner well into the XAD-2 module using a Teflon wash bottle containing methylene chloride, so that the rinse travels down the module and into the condensate collector. Then remove the well entirely and place to one side on a clean surface (aluminum foil pre-rinsed with methylene chloride). Rinse the entrance tube into the module interior; rinse the condenser wall allowing solvent to flow down through the system and collect in the condensate cup.

9. Release the central clamp again and separate the lower section (XAD-2 cartridge holder and condensate cup) from the upper.

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[1] For safety, the tip of the separatory funnel should always be directed away from the face and eyes while venting.

10. Lift the empty XAD-2 cartridge halfway out of the mid-section and rinse the outer surface down into the condensate cup. Remove the cartridge completely to a clean surface (aluminum foil rinsed with methylene chloride).

11. Rinse the empty XAD-2 section into the condensate cup. Open the condensate reservoir valve and drain into the XAD-2 sample storage container (wide-mouth amber glass jar).

12. Rinse the condensate reservoir and combine the rinse with the XAD-2 resin as above.

13. Clearly label all containers according to the coding scheme presented in Table 2; cover each label completely with transparent tape; mark liquid levels and store all liquid samples on ice.

Impingers

Sample recovery from the impingers may also be accomplished independently of the other two sections of the SASS train. The procedures is described below:

First Impinger

1. Measure the volume of liquid in the impinger with a graduated cylinder; combine with the aqueous residue from the condensate.

2. Rinse the line connecting the XAD-2 module to the first impinger with distilled water; transfer the rinse to the same graduated cylinder. Rinse the impinger twice more with distilled water, combining all rinses in the graduated cylinder. Measure the total rinse volume and add to the sample. Rinse the graduated cylinder with a known amount of distilled water and add to the sample. Record all volumes on the sample recovery sheet.

Second and Third Impingers

1. Measure and record the combined volume of liquid in the impingers in a large (1,000 ml) graduated cylinder; transfer to a clean sample storage container.

2. Rinse the line connecting the first and second impinger into the second impinger and the line connecting the second and third impinger into the third impinger. Transfer the rinses to the same graduated cylinder. Rinse each impinger twice again with distilled water, combining all rinses in the graduated cylinder.

Measure and record the combined rinse volume and add to the sample. Rinse the graduated cylinder with a known amount of distilled water and add to the sample. Record this additional rinse volume and add to the impinger rinse volume above.

3. Clearly label all sample containers according to the coding scheme presented in Table 4; cover each label completely with transparent tape; mark fluid levels and store all liquid samples on ice.

Fourth Impinger

1. Transfer the silica gel to its original container. Weigh to the nearest 0.1 gram on a triple-beam balance, and record the weight obtained.

2. Discard or regenerate.

Sample Preparation for Shipment

Prior to shipment, recheck all sample containers to insure that the caps are securely tightened. Seal the lids of all nalgene containers around the circumference with vinyl tape and those of glass containers wiht Teflon tape. Ship all liquid samples on ice and all particulate filters with the particulate catch facing upward. Ship peroxide solutions (impinged) in a separate container.

Calibration

All calibration results should be recorded on an appropriate data sheet and fastened securely into a separate section in the field sampling notebook. Samples of blank data appear in 40 CFR 60, Appendix A.

Probe Nozzles

Probe nozzles must be calibrated before each initial use in the field. Using vernier calipers,[1] measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Perform ten separate measurements using different diameters; obtain the average of the ten measurements. The difference between the high and low measurement results must not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they must be reshaped, sharpened and recalibrated before reuse. Recalibration of the nozzle is strongly recommended before each run in gas streams that are highly corrosive

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[1] Or micrometers.

corrosive as the nozzle diameter may be changing slightly from one run to the next. Each nozzle must be permanently and uniquely engraved.

Pitot Tube

If the Type-S pitot tube conforms to the construction specifications (the face openings are not visibly nicked, dented, or corroded) and the pitot tube/probe assembly meets the intercomponent spacings outlined in EPA Method 2, the pitot tube need not be calibrated to meet federal and many state testing requirements; a correction coefficient may be assigned in these cases. Some states, however, require that, once used, pitot tubes must be calilbrated in a wind tunnel. Specific state requirements such as this must be unequivocally stated prior to testing. In either case, pitot tube face openings should be visually impacted before each run to insure that there has been no change in appearance since their construction or most recent calibration.

Metering System

Before each initial use in the field, the metering system shall be calibrated using a standard bell prover of the proper size.[1] A meter stick should be used to indicate the distance travelled by the inner tank during the measurement. Figure 1.2.1.9-5 illustrates a suitable arrangement for the calibration. It is highly recommended that the dry gas meter be adjusted until the ratio of the dry gas meter volume to the standard bell prover volume equals 1.00 ± 0.01 to insure that the calculated ΔH_i will result in near-isokinetic sampling rates. The calibration procedure follows:

1. Perform both a positive (pressure) and a negative (vacuum) leak check of the metering system. For the negative leak check, include only the orifice magnehelics, dry gas meter and two vacuum pumps by removing the vacuum line connecting the fourth impinger to the vacuum pumps at the common side of the pump inlet tee, and replacing the line with a plain-end male quick connect. Tightly cap this end and leak check in the manner outlined under Preparation of the Collection Train.

   For the positive leak check, connect a short length of rubber tubing to the "gas exhaust" port on the SASS control module; disconnect and vent the low side of the orifice magnehelic; close off the low-side orifice tap; pressurize the system to 13-18 cm H_2O (5-7 in. H_2O) by blowing into the rubber tubing; pinch off the tubing and observe the magnehelic for one minute; the magnehelic reading must remain unchanged during that time period. Any loss of magnehelic pressure indicates a leak that must be corrected.

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[1] A standard bell prover is recommended for this procedure because the displacement volume of commercially available wet test meters is typically insufficient.

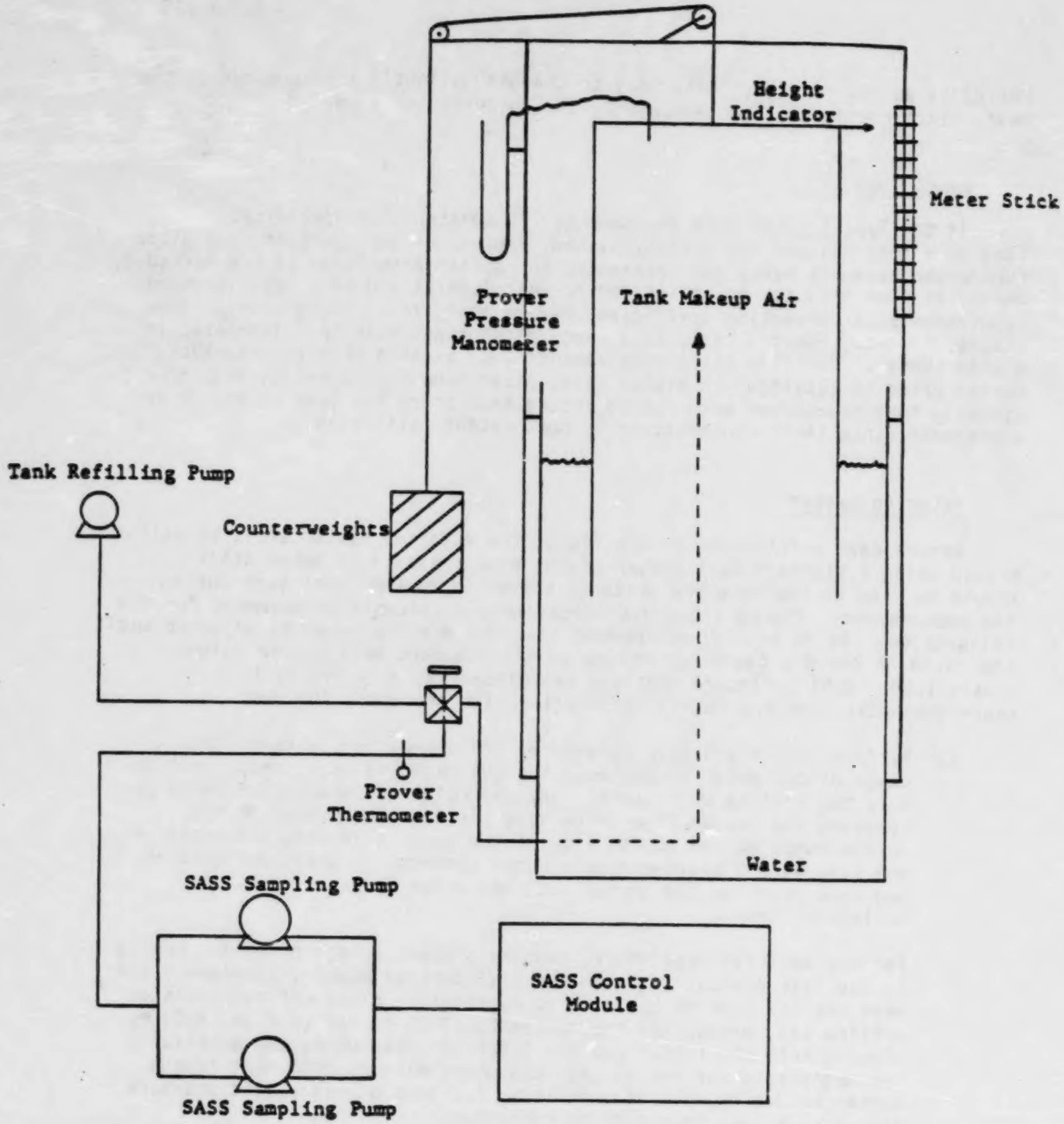
Height Indicator
Meter Stick
Prover Pressure Manometer
Tank Makeup Air
Tank Refilling Pump
Counterweights
Prover Thermometer
Water
SASS Sampling Pump
SASS Control Module
SASS Sampling Pump

Figure 1.2.1.9 - 5. Schematic Diagram of Standard Bell Prover Arrangement for SASS Dry Gas Meter Calibration.

2. Upon obtaining satisfactory leak checks, connect the metering system to the standard bell prover.

3. Using the control box magnehelic indicator, set the pumping rate corresponding to a ΔH of 1 in. Hg. Turn the pumps off using the switches.

4. Record the initial temperature and pressure of the bell prover and the initial temperature and reading of the dry gas meter. Record the barometric pressure every hour.

5. Disconnect the metering system and pump the inner tank of the bell prover to a convenient height. Reconnect the metering system and record the height.

6. Start the pumps and a stopwatch simultaneously; evacuate the tank for 3 minutes.

7. After 3 minutes, turn off the pumps using the switches. Record the final inner tank height, the final dry gas meter reading and temperature, and the bell prover final temperature and pressure.

8. Repeat steps 3-7 using ΔH settings of 2, 4, and 6 in. H_2O.

9. Duplicate the entire procedure as a check; repeat the entire procedure after each adjustment of the dry gas meter.

10. Calculate the Dry Gas Meter Correction Coefficient, the ratio of the volume of gas measured by the dry gas meter to the standard bell prover, both corrected to standard conditions and on a dry basis. The ratio reduces to:

$$\gamma = \frac{V_{dgm(std)}}{V_{pvr(std)}} = \frac{V_{dgm} P_{dgm} T_{pvr}}{V_{pvr} P_{pvr} T_{dgm}}$$

where:

γ = Dry gas meter correction coefficient, dimensionless.

$V_{dgm(std)}$ = Volume of gas measured by the dry gas meter on a dry basis, corrected to standard conditions, dscm (dscf).

$V_{pvr(std)}$ = Volume of gas measured by the standard bell prover on a dry basis, corrected to standard conditions, dscm (dscf).

V_{dgm} = Volume of gas measured at dry gas meter conditions, $m^3(ft^3)$.

= final volume reading - initial volume reading

V_{prv} = Volume of gas measured at standard bell prover conditions, $m^3(ft^3)$.

= K_{pvr}x (difference in meter stick height readings).

where:

K_{pvr} = number of cubic feet of air displaced represented by each cm of movement along the meter stick, $m^3/cm(ft^3/cm)$.

P_{dgm} = Absolute meter pressure, mm Hg (in. Hg).

$$= \text{Barometric pressure} + \frac{\Delta H}{13.6}$$

P_{pvr} = Absolute prover pressure, mm Hg (in. Hg).

$$= \text{Barometric pressure} - \frac{(\Delta P)\text{ prover manometer}}{13.6}$$

T_{pvr} = Absolute bell prover temperature, °K (°R).

T_{dgm} = Absolute dry gas meter temperature, °K (°R).

11. Calculate the Orifice Constants using the following equations:

(a) $$Q_{mo} = (1-B_{ws})Q_{std} \frac{P_{std}T_{m(avg)}}{P_mT_{std}}$$

where:

Q_{mo} = Sampling flowrate at orifice, ft^3/min (dry).

B_{ws} = Proportion by volume of water in ambient air, dimensionless.

Q_{std} = Standard sampling flowrate for SASS, 4.0 scfm (wet).

P_{std} = Standard absolute pressure, 29.92 in. Hg.

$T_{m(avg)}$ = Average meter temperature, °R.

P_m = Absolute meter pressure (barometric pressure + $\Delta H/13.6$), in. Hg.

T_{std} = Standard temperature, 528° R.

(b)
$$J_i = \frac{Q_{mo}}{A_{oi}} \left[\frac{T_{m(avg)}}{P_m M_m} R \Delta H_i 2g_c \right]^{-1/2}$$

where

J_i = Orifice coefficient for orifice "i".

Q_{mo} = Sampling flowrate at orifice, ft^3/min (dry).

A_{oi} = Orifice area $\frac{\pi(\text{diameter})^2}{4}$, $in.^2$

$T_{m(avg)}$ = Average meter temperature, °R.

P_m = Absolute meter pressure (see equation above), in. Hg.

M_m = Molecular weight of air, 29.0 lb_m/lb-mole.

R = Gas law constant, 1545 ft-lb_f/°R lb-mole.

ΔH_i = Orifice "i" pressure drop, in. H_2O.

g_c = Gravitational constant, 32.17 lb_m-ft/lb_f sec^2.

The orifice constants may be determined without the bell prover by noting the dry gas meter volumes obtained by pumping at 1, 2, 3, and 6 in. H_2O for 3-minute periods. Checking orifice constants in the field and obtaining consistent values for these may be used as a rough indication of a valid calibration during extended field use.

After each series of field tests, the calibration of the metering system must be checked by performing three calibration measurements at a single intermediate orifice setting at or near the average used during the field testing. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings. Calculations for the test series should then be performed using whichever calibration results in the lower value for total sample volume.

Probe Heater

The probe heating system shall be calibrated before each initial use in the field and checked after each series of field tests according to the procedure outlined in APTD-0576.

Thermocouples

Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM-E-1 #63C or 63F specifications. Thermocouples should be calibrated in the laboratory without the use of extension leads. If extension leads are used in the field, the thermocouple reading at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5%.

Impinger and Organic Module Thermocouples

For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, a three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ± 2° C (3.6° F) with those of the absolute value of the reference thermometer.

Dry Gas Meter Thermocouples

For the thermocouples used to indicate the dry gas meter inlet and outlet temperatures, a three-point calibration at ice-water, room air, and boiling water temperatures must be performed. The values must be within ± 2° C (3.6° F) of the absolute reference thermometer value at all three calibration points.

Probe and Stack Thermocouple

For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling water, and boiling coking oil temperatures must be performed; it is highly recommended that room air temperature be added as a fourth calibration point. If the absolute values of the reference thermometer and the thermocouple agree within 1.5% at each of the calibration points, a calibration curve (equation) may be constructed (calculated), and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

Barometer

Adjust the field barometer initially and before each test series to agree within ± 2.5 mm Hg (0.1 in. Hg) of the mercury barometer, or within the station barometric pressure value reported by a nearby National Weather Service station and corrected for elevation.

Triple-Beam Balance

Calibrate the triple beam balance before each test series using Class-S standard weights; the weights must be within ± 0.5 g of the standards, or the balance adjusted to meet these limits.

Analytical Balance

Calibrate the analytical balance with Class-S weights before initially tare weighing each set of filters. The balance must agree or be adjusted to within ± 2 mg of the standards. Run at least one standard each time one or more of the filters is reweighed.

Calculations

Dry Gas Volume

1. From the SASS run sheet, average the dry gas meter temperatures and orifice pressure drops readings throughout the run.
2. Calculate the Volume of Dry Gas Sampled at standard conditions: (20° C, 760 mm Hg; 528° R, 29.92 in. Hg) using the equation:

$$V_{m(std)} = V_m \gamma \frac{(T_{std})}{T_m} \frac{(P_{bar} + (\Delta H/13.6))}{P_{std}}$$

$$= K_i V_m \gamma \frac{(P_{bar} + (\Delta H/13.6))}{T_m}$$

where:

$V_{m(std)}$ = Volume of dry gas sampled at standard conditions, dscm (dscf).

V_m = Volume of dry gas sampled at dry gas meter conditions, dcm (dcf).

γ = Dry gas meter calibration factor, dimensionless.

T_m = Average dry gas meter temperature, °K (°R).

T_{std} = Standard absolute temperature, °K (°R).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, mm Hg (in. Hg).

ΔH = Average orifice pressure drop during the sampling run, mm H_2O (in. H_2O).

K_1 = 0.358 °K/mm for metric units.

= 17.64 °R/in. Hg for English units.

The above equation must be modified whenever the leakage rates observed during any of the mandatory leak checks (i.e., the post-test leak checks or leak checks made prior to component changes) exceed the maximum allowed. The modification follows:

(a) Case I. No component changes have been made during the sampling run, and the allowable leakage rate has been exceeded during the post-test leak check.

Replace V_m with the expression:

$$V_m - \left[(L_p - L_a)\theta \right]$$

where

L_p = Leakage rate observed during post-test leak check, m^3/min (cfm).

L_a = Maximum allowed leakage rate, 0.0014 m^3/min (0.05 ft^3/min).

θ = Total sampling time, min.

(b) Case II. One or more component changes made during the sampling run, and the allowable leakage rate has been exceeded during one or more of the leak checks prior to component changes or during the post-test leak check.

Replace V_m with the expression:

$$V_m - \left[\sum_{i=1}^{n} (L_i - L_a)\,\theta_{i-1} - (L_p - L_a)\,\theta_p \right]$$

where:

L_i = Leakage rate observed prior to "ith" component change if the allowable leakage rate has been exceeded while sampling with the "ith" component, m^3/min (cfm).

L_a = Maximum allowed leakage rate, 0.0014 m^3/min (0.05 ft^3/min).

θ_{i-1} = Sampling time interval between the successive component changes in which the allowable leakage rate has been exceeded, min.

L_p = Leakage rate observed during post-test leak check, if the allowable leakage rate has been exceeded, m^3/min (cfm).

θ_p = Sampling time interval, from the final (nth) component change until the end of the sampling run, if the allowable leakage rate has been exceeded during the post-test leak check, min.

Moisture Content

1. Calculate the Volume of Water Vapor at standard conditions.

$$V_{w(std)} = \frac{V_{1c}\rho_w}{P_{std}} = K_2 V_{1c}$$

where:

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf).

V_{1c} = Volume of liquid collected in the condensate reservoir added to the net increase in impinger solution volumes and silica gel weight gain during the run, ml.

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

M_w = Molecular weight of water, 18.0 g/g-mole (lb/lb-mole).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_{std} = Standard absolute temperature, °K (°R).

P_{std} = Standard absolute pressure, mm Hg (in. Hg).

K_2 = 0.001333 m^3/ml for metric units.

= 0.04707 ft^3/ml for English units.

2. Calculate the Stack Gas Moisture Content[1]

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

where:

B_{ws} = Proportion of water vapor in the gas stream by volume, dimensionless.

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf).

$V_{m(std)}$ = Volume of gas measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

In saturated or water droplet-laden gas streams, make two calculations of the moisture content, one from the total volume of liquid collected in the train and one from the assumption of saturated gas streams conditions. Use whichever method results in the lower value. To determine the moisture content based upon saturated conditions, use the average stack gas temperature in conjunction with: (1) a psychrometric chart, correcting for difference between the chart and the absolute stack pressure, or (2) saturation vapor pressure tables.

Particulate Concentration

1. Calculate the Unit Methanol/Methylene Chloride Blank Correction for all front-half samples.

$$C_{mm} = \frac{M_{mm}}{V_{mm} \rho_{mm}}$$

---

[1] The Stack Gas Moisture Content equals B_{ws} times 100 for conversion to percent.

where:

C_{mm} = Methanol/methylene chloride blank correction, mg/g.

M_m = Mass of methanol/methylene chloride after evaporation, mg.

V_{mm} = Volume of methanol/methylene chloride used in wash, ml.

ρ_{mm} = Density of 50:50 mix of methanol/methylene chloride, mg/ml (see labels on bottles).

2. Calculate the Total Methanol/Methylene Chloride Blank Weight Correction for each individual front-half sample.

$$W_{mm} = C_{mm} V_{mm} \rho_{mm}$$

where:

W_{mm} = Weight of residue in methanol/methylene chloride front-half wash, mg.

C_{mm} = Methanol/methylene chloride unit blank correction, mg/g.

V_{mm} = Volume of methanol/methylene chloride used for front-half wash, ml.

ρ_{mm} = Density of 50:50 mixture of methanol and methylene chloride, mg/ml.

3. Calculate Total Particulate Weight.

$$W_p = (W_{pf-a} + W_{pf-b} + \ldots\ldots.) + (W_{10c} + W_{3c} + W_{1c}) + (W_{pr} - W_{mm})$$

where:

W_p = Total particulate weight, mg.

$W_{pf-a}+\ldots$ = Particulate weight from filter PF-a+PF-b+...

$W_{10c}, W_{3c} W_{1c}$ = Particulate weight catch from the 10-, 3-, and 1-μm cyclones respectively, mg.

W_{pr} = Weight of front-half rinse residue before blank correction, mg.

W_{mm} = Methanol/methylene chloride blank weight correction, mg.

4. Calculate the Total Particulate Concentration.

$$C_p = (0.001\ \text{g/mg})\ (W_p/V_{m(std)})$$

where:

C_p = Concentration of particulate material in the stack gas, g/dscm (gr/dscf).

W_p = Weight of particulate material collected during run, mg.

$V_{m(std)}$ = Volume of gas sampled, dscm (dscf).

To convert the above concentration to units of gr/ft^3 or lb/ft^3 for comparison with established or projected values, the following conversion factors are useful:

From	To	Multiply By
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft	2.205×10^{-3}
g/ft^3	g/m^3	35.315

Concentration of Organic Material

1. Calculate the Volumetric Flow Rate (Q_{sd}) during the run. Determine the average stack gas velocity and volumetric flow rate from actual run data in the same manner that these were calculated during preliminary determinations (see section on Preliminary Field Determinations).

2. Calculate the POHC Concentration:

$$C_{pohc} = \frac{M_{pohc}}{Q_{sd}} = \frac{M_{cd\text{-}le} + M_{mrx}}{Q_{sd}}$$

where:

C_{pohc} = Concentration of POHC's in stack gas, µg/dscm.

M_{pohc} = Total mass of POHC's collected in XAD-2 and organic module rinse, and in the condensate extract, µg.

M_{cd-le} = Mass of POHC's extracted from the condensate (corrected for methylene chloride blank extraction residue), µg.

M_{mrx} = Mass of POHC's extracted from the XAD-2 sorbent and organic module rinse (corrected for methylene chloride blank extraction residue), µg.

Q_{sd} = Volumetric flow rate during the run, dscm.

Isokinetic Variation

1. Having calculated T_s, $V_{m(std)}$, V_s, A_n, P_s, and B_{ws}, determine the Isokinetic Variation using the equation:

$$I = K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$

where:

I = Isokinetic variation, %.

T_s = Absolute average stack gas temperature (°K (°R).

$V_{m(std)}$ = Volume of gas sampled, dscm (dscf).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

V_s = Stack gas velocity, m/sec (ft/sec).

A_n = Cross-sectional area of nozzle, $m^3 (ft^3)$.

θ = Net sampling time, min.

B_{ws} = Proportion of water vapor in gas stream by volume, dimensionless.

K_4 = 4.320 for metric units.

= 0.09450 for English units.

- For the accuracy of Level 1 requirements (factor of 3) for measured particulate emissions, the isokinetic variation must be within 70-150%.

Cyclone Particle Size Cutoff Diameter[1]

The range of particle size collected in each cyclone and on the filter is dependent upon the operating temperature and flow rate through each of these components. The particle size cutoff diameters of 10-, 3-, and 1-μm in the cyclones are the result of calibration of these at 400° F and 4.0 scfm (6.5 acfm). When the determined isokinetic sampling rate is not 4.0 scfm, or it is necessary to maintain a constant subisokinetic sampling rate (still within the limits of Level 1 accuracy) during the SASS run, the particle size cutoff diameters for the cyclones must be extrapolated.

Existing calibration data is insufficient to determine exact mathematical relationships for the variation of particle size cutoff diameter with temperature and volumetric flow rate. The best estimates[2] suggest that a square, and an inverse square root dependence, respectively, exist; the extrapolation equation is presented below:

1. Calculate the Gas Viscosity from the equation:

$$\mu = (1.68 \times 10^{-4}) + (2.292 \times 10^{-7})\,(T)$$

where:

μ = Gas viscosity, poise.

T = Gas temperature, °F.

2. Extrapolate the Particle Size Cutoff Diameter from:

$$D_{T_a,F_a} = D_{400,4.0}\,\frac{\left(\dfrac{\mu_{400}}{\mu_{T_a}}\right)^2}{\left(\dfrac{V_{4.0}}{V_{F_a}}\right)^{1/2}} = D_{400,4.0}\,\frac{3.37\sqrt{V_{F_a}}}{\mu^2_{T_a}}$$

---

[1] The particle size cutoff diameter represents that particle diameter (assuming spherical particles of unit density) at which the cyclone exhibits 50% collection efficiency, and is expressed as the "d_{50}."

[2] Source: Private communication with J.D. McCain of Southern Research Institute, 2000 South Ninth Avenue, Birmingham, Alabama 35205.

where:

D_{T_a,F_a} = Particle size cutoff diameter at cyclone operating temperature and flow rate, µm[1].

$D_{400,4.0}$ = Particle size cutoff diameter at an operating temperature of 400° F and flow rate of 4.0 scfm, µm.

μ_{400} = Gas viscosity at 400° F, poise.

μ_{T_a} = Gas viscosity at operating conditions, poise.

$V_{4.0}$ = Cyclone volumetric flow rate of 4.0 scfm.

V_{F_a} = Cyclone volumetric flow rate at operating conditions, scfm.

This equation reduces to:

$$\frac{33.7\sqrt{V_{F_a}}}{\mu_{T_a}^{2}} \quad \text{for the 10-µm cyclone.} \tag{1}$$

$$\frac{10.1\sqrt{V_{F_a}}}{\mu_{T_a}^{2}} \quad \text{for the 3-µm cyclone.} \tag{2}$$

$$\frac{3.37\sqrt{V_{V_a}}}{\mu_{T_a}^{2}} \quad \text{for the 1-µm cyclone.} \tag{3}$$

---

[1] Note that the volumetric flow rate must be corrected to standard conditions.

Cumulative Particulate Weight Percent Less Than Calculated Size

1. Divide the weight collected in the individual cyclones and on the filter by the total weight of particulate collected; express these as a percentage, using the following equations:

$$\% W_{pf} = \frac{W_{pf-a} + W_{pf-b} + \ldots}{W_p} \times 100$$

$$\% W_{10c} = \frac{W_{10c}}{W_p} \times 100$$

$$\% W_{3c} = \frac{W_{3c}}{W_p} \times 100$$

$$\% W_{1c} = \frac{W_{1c}}{W_p} \times 100$$

where:

W_p = Total particulate weight collected, mg.

W_{pf} = $W_{pf-a} + W_{pf-b} + \cdots$ = Particulate weight collected on filters PF-a + PF-b, etc., mg.

W_{10c} = Particulate weight collected in 10-µm cyclone, mg.

W_{3c} = Particulate weight collected in 3-µm cyclone, mg.

W_{1c} = Particulate weight collected in 1-µm cyclone, mg.

100 = Conversion to percent.

2. Calculate the Cumulative Weight Percent Less than the Calculated Particle Size Cutoff Diameter by adding, to each weight percent, the weight percent of all fractions having a smaller particle size cutoff diameter. Tabularize the data, using the form below as an example:

PRESENTATION OF SASS PARTICLE SIZING DATA

Stage	Weight % Collected in Stage	Cumulative Weight % Less than Calculated Particle Size Cutoff Diameter	Calculated Particle Size Cutoff Diameter
10-µm cyclone			
3-µm cyclone			
1-µm cyclone			
Glass fiber filter			

1.2.1.9.1 References

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1.2.1.13 Sample Collection for the Determination of the Emissions of Volatile Organic Compounds from Hazardous Waste Incinerators

Scope and Application

This method describes the collection of volatile principle organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators. For the purpose of definition, volatile POHCs are those POHCs with boiling points less than 100° C. If the boiling point of a POHC of interest is less than 30° C, the POHC may break through the sorbent under the conditions of the sample collection procedure. Field application for POHCs of this type should be supported by laboratory data which demonstrates the efficiency of a volatile organic sampling train (VOST) to collect POHCs with boiling points less than 30° C. This may require using reduced sample volumes collected at flow rates between 250 and 500 ml/min. Also, many compounds which boil above 100° C (e.g., chlorobenzene) may be efficiently collected and analyzed using this method. VOST collection efficiency for these compounds should be demonstrated, where necessary, by laboratory data of the type described above. This method employs a 20-liter sample of effluent gas containing volatile POHCs which is withdrawn from a gaseous effluent source at a flow rate of 1 liter per minute, using a glass-lined probe and a volatile organic sampling train (VOST). (Operation of the VOST under these conditions has been called FAST-VOST). The gas stream is cooled to 20° C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent resin traps. Liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap (front trap) contains approximately 1.6 g Tenax and the second trap (back trap) contains approximately 1 g each of Tenax and petroleum-based charcoal (SKC Lot 104 or equivalent), 3:1 by volume. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

An alternative set of conditions for sample collection has been used. This method involved collecting sample volume of 20 liters or less at reduced flow rate. (Operation of the VOST under these conditions has been referred to as SLO-VOST.) This method has been used to collect 5 liters of sample (0.25 liter/min for 20 min) or 20 liters of sample (0.5 liter/min for 40 min) on each pair of sorbent cartridges. Smaller sample volumes collected at lower flow rates should be considered when the boiling points of the POHCs of interest are below 35° C. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

Analysis of the traps is carried out by thermal desorption, purge and trap by gas chromatography/mass spectrometry (see Method 3720). The VOST is designed to be operated at 1 liter/min with traps being replaced every 20 minutes for a total sampling time of 2 hr. Traps may be analyzed separately or combined onto one trap to improve detection limit. However, additional flow rates and sampling times are acceptable. Recent experience has shown that when less than maximum detection ability is required, it is acceptable and probably preferable to operate the VOST at 0.5 liter/min for a total of three 40-min periods. This preserves the 2-hr sampling period, but reduces the number of cartridge changes in the field as well as the number of analyses required.

This method is applicable to the determination of volatile POHCs in the stack gas effluent of hazardous waste incinerators. This method is designed for use in calculating the destruction and removal efficiency (DRE) for the volatile POHCs and to enable determination that DRE values for removal of the volatile POHCs is equal to or greater than 99.99 percent (1).

The sensitivity of this method is dependent upon the level of interferences in the sample and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of this method is 0.1 micrograms per cubic meter ($\mu g/m^3$) of flue gas (0.1 nanograms per liter [ng/l]) to permit calculation of a DRE equal to or greater than 99.99 percent for volatile POHCs which may be present in the waste stream at 100 parts per million (ppm). The upper end of the range of applicability of this method is limited by breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Laboratory development data (2) have demonstrated a range of 0.1 to 100 $\mu g/m^3$ (0.1 to 100 ng/l) for selected volatile POHCs collected on a pair of sorbent traps using a total sample volume of 20 liters or less (see discussion of SLO-VOST method).

This method is recommended for use only by experienced sampling personnel and anaytical chemists or under close supervision by such qualified persons.

Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many potential interferences can be due to exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile POHCs in the ambient air at hazardous waste incinerator sites.

To avoid or minimize the low-level contamination of train components with volatile POHCs, care should be taken to avoid contact of all interior surface or train components with synthetic organic materials (e.g., organic solvents, lubricating and sealing greases) and train components should be carefully cleaned and conditioned according to the procedures described in this protocol.

Apparatus

Volatile Organic Sampling Train

A schematic diagram of the principle components of the VOST is shown in Figure 1.2.1.13-1 and a diagram of one acceptable version of VOST is shown in Figure 1.2.1.13-2. The VOST consists of a glass-lined probe, followed by an isolation valve,a water-cooled glass condenser, a sorbent cartridge containing

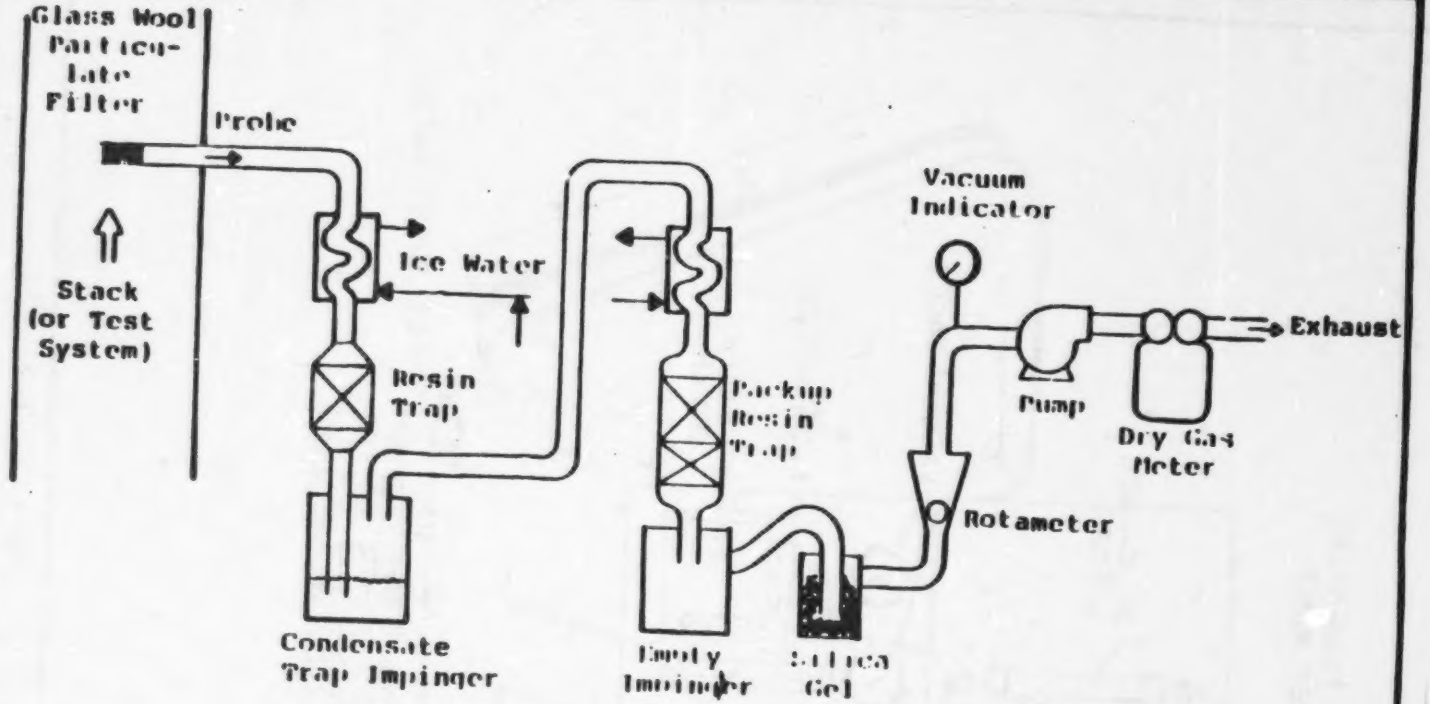

Glass Wool
Particulate Filter
Probe
Stack (or Test System)
Ice Water
Resin Trap
Condensate Trap Impinger
Backup Resin Trap
Empty Impinger
Silica Gel
Vacuum Indicator
Rotameter
Pump
Dry Gas Meter
Exhaust

Figure 1.2.1.13 - 1
SCHEMATIC OF
VOLATILE ORGANIC SAMPLING TRAIN
(VOST)

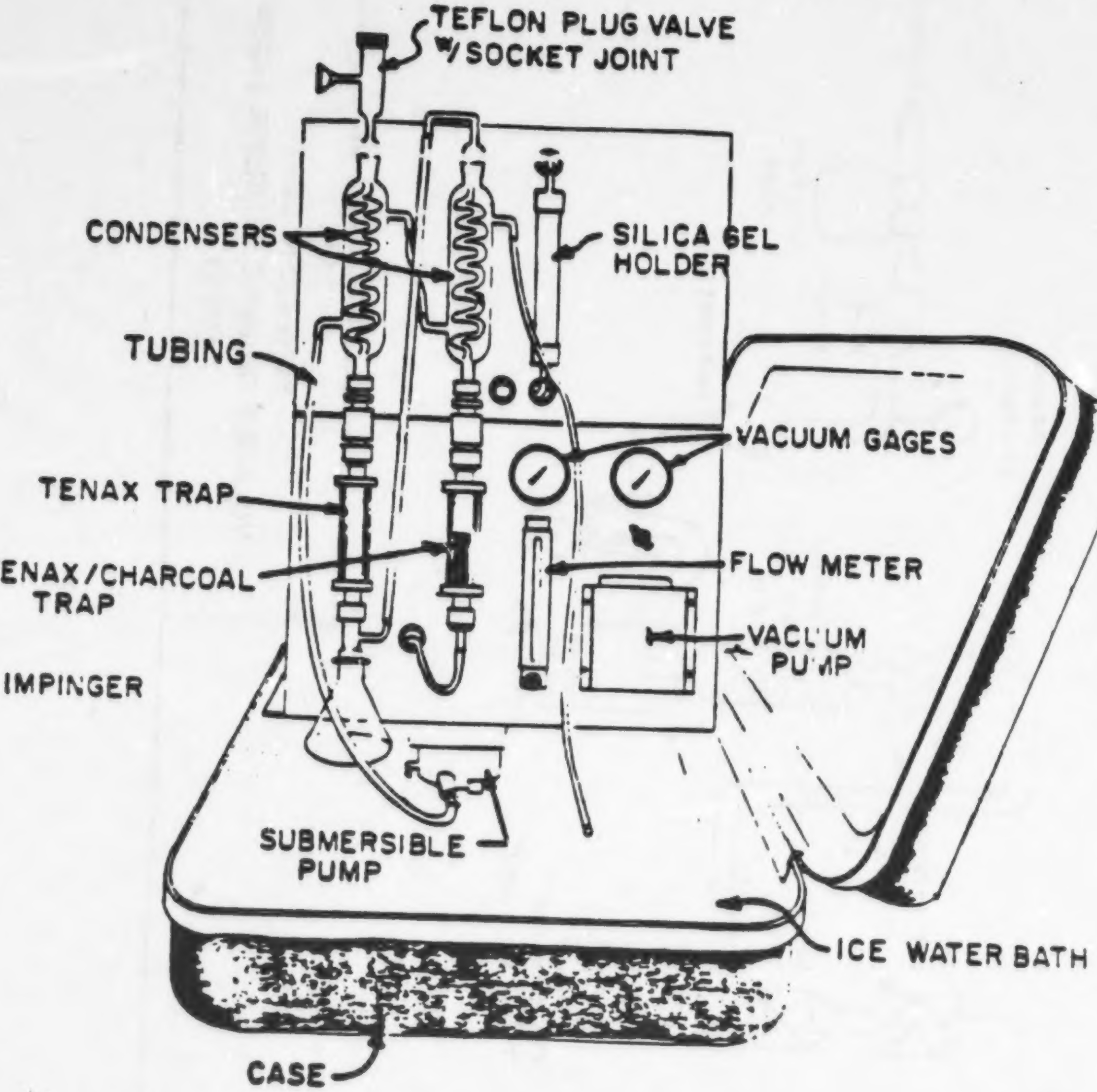

TEFLON PLUG VALVE
W/ SOCKET JOINT
CONDENSERS
SILICA GEL
HOLDER
TUBING
VACUUM GAGES
TENAX TRAP
TENAX/CHARCOAL
TRAP
FLOW METER
VACUUM
PUMP
IMPINGER
SUBMERSIBLE
PUMP
ICE WATER BATH
CASE

Figure 1.2.1.13 - 2

(VOST)

VOLATILE ORGANIC SAMPLING TRAIN

Tenax (1.6 g), an empty impinger for condensate removal, a second water-cooled glass condenser, a second sorbent cartridge containing Tenax and petroleum-based charcoal (3:1 by volume; approximately 1 g of each), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter.

The gas pressure during sampling and for leak checking is monitored by pressure gauges which are in line and downstream of the silica gel drying tube.

Probe

The probe should be made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is to be maintained above 130° C but low enough to ensure a resin temperature of 20° C. A water-cooled probe may be required at elevated stack temperatures to protect the probe and meet the above requirements. Isokinetic sample collection is not a requirement for the use of VOST since the compounds of interest are in the vapor phase at the point of sample collection.

Isolation Valve

The isolation valve should be a greaseless stopcock with a glass bore and sliding Teflon plug with Teflon wipers (Ace 8193 or equivalent).

Condensers

The condensers (Ace 5979-14 or equivalent) should be of sufficient capacity to cool the gas stream to 20° C or less prior to passage through the first sorbent cartridge. The top connection of the condenser should be able to form a leak-free, vacuum-tight seal without using sealing greases.

Sorbent Cartridges

The sorbent cartridges used for the VOST may be used in either of two configurations: the inside-outside (I/O) configuration in which the cartridge is held within an outer glass tube and in a metal carrier, and the inside-inside (I/I) configuration in which only a single glass tube is used, with or without a metal carrier. In either case, the sorbent packing will be the same. The first of a pair of sorbent cartridge shall be packed with approximately 1.6 g Tenax GC resin and the second cartridge of a pair shall be packed with Tenax GC and petroleum-based charcoal (3:1 by volume; approximately 1 g of each).

The second sorbent cartridge shall be packed so that the sample gas stream passes through the Tenax layer first and then through the charcoal layer.

The sorbent cartridges shall be glass tubes with approximate dimensions of 10 cm by 1.6 cm I.D. The two acceptable designs (I/O, I/I) for the sorbent cartridge are described in further detail below.

Inside/Inside Sorbent Cartridge

A diagram of an I/I sorbent cartridge is shown in Figure 1.2.1.13-3. This cartridge is a single glass tube (10 cm by 1.6 cm I.D.) which has the ends reduced in size to accommodate a 1/4- or 3/8-inch Swagelok or Cajon gas fitting. The resin is held in place by glass wool at each end of the resin layer. The amounts of each type of sorbent material used in the I/I design are the same as for the I/O design. Threaded end caps are placed on the sorbent cartridge after packing with sorbent to protect the sorbent from contamination during storage and transport.

Inside/Outside Type Sorbent Cartridge

A diagram of an I/O sorbent cartridge is shown in Figure 1.2.1.13-4. In this design the sorbent materials are held in the glass tube with a fine mesh stainless steel screen and a C-clip. The glass tube is then placed within a larger diameter glass tube and held in place using Viton O-rings. The purpose of the outer glass tube is to protect the exterior of the resin-containing tube from contamination. The two glass tubes are held in a stainless steel cartridge holder where the ends of the glass tubes are held in place by Viton O-rings placed in machine grooves in each metal end piece. The three cylindrical rods are secured in one of the metal end peices and fastened to the other end piece using knurled nuts, thus sealing the glass tubes into the cartridge holder. The end pieces are fitted with a threaded nut onto which a threaded end cap is fitted with a Viton O-ring seal to protect the resin from contamination during transport and storage.

Metering System

The metering system for VOST shall consist of vacuum gauges, a leak-free pump (Thomas Model 107 or equivalent, Thomas Industries, Sheboygan, WI), a calibrated rotameter (Linde Model 150, Linde Division of Union Carbide, Keasbey, NJ) for monitoring the gas flow rate, a dry gas meter with 2 percent accuracy at the required sampling rate and related valves and equipment.

Provisions should be made for monitoring the temperature of the sample gas stream between the first condenser and first sorbent cartridge. This can be done by placing a thermocouple on the exterior glass surface of the outlet from the first condenser. The temperature at that point should be less than 20° C. If it is not, an alternative condenser providing the required cooling capacity must be used.

Sample Transfer Lines

All sample transfer lines to connect the probe to VOST shall be less than 5 ft in length, and shall be heat-traced Teflon with connecting fittings which are capable of forming leak-free, vacuum-tight connections without the use of sealing grease. All other sample transfer lines used with the VOST shall be Teflon with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

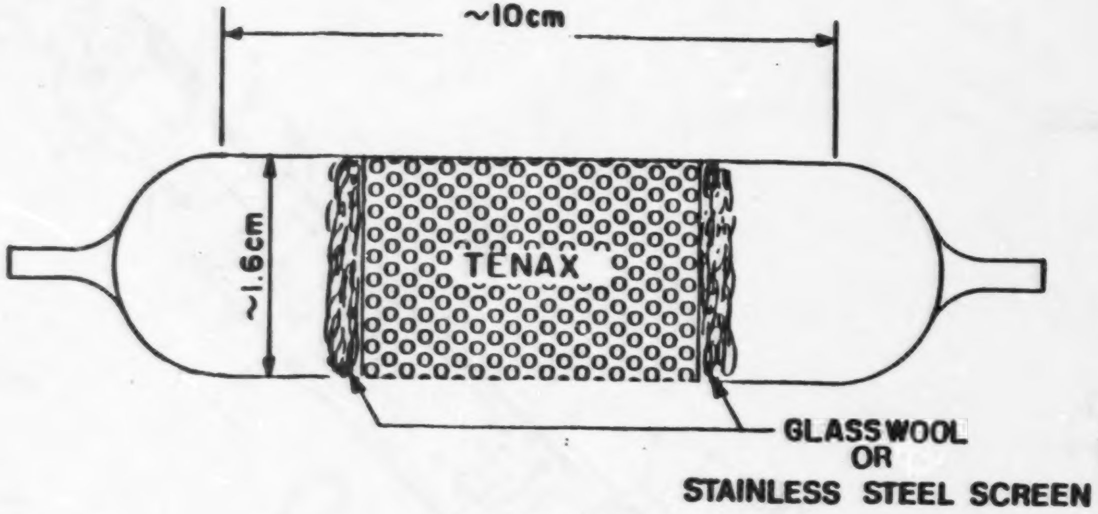
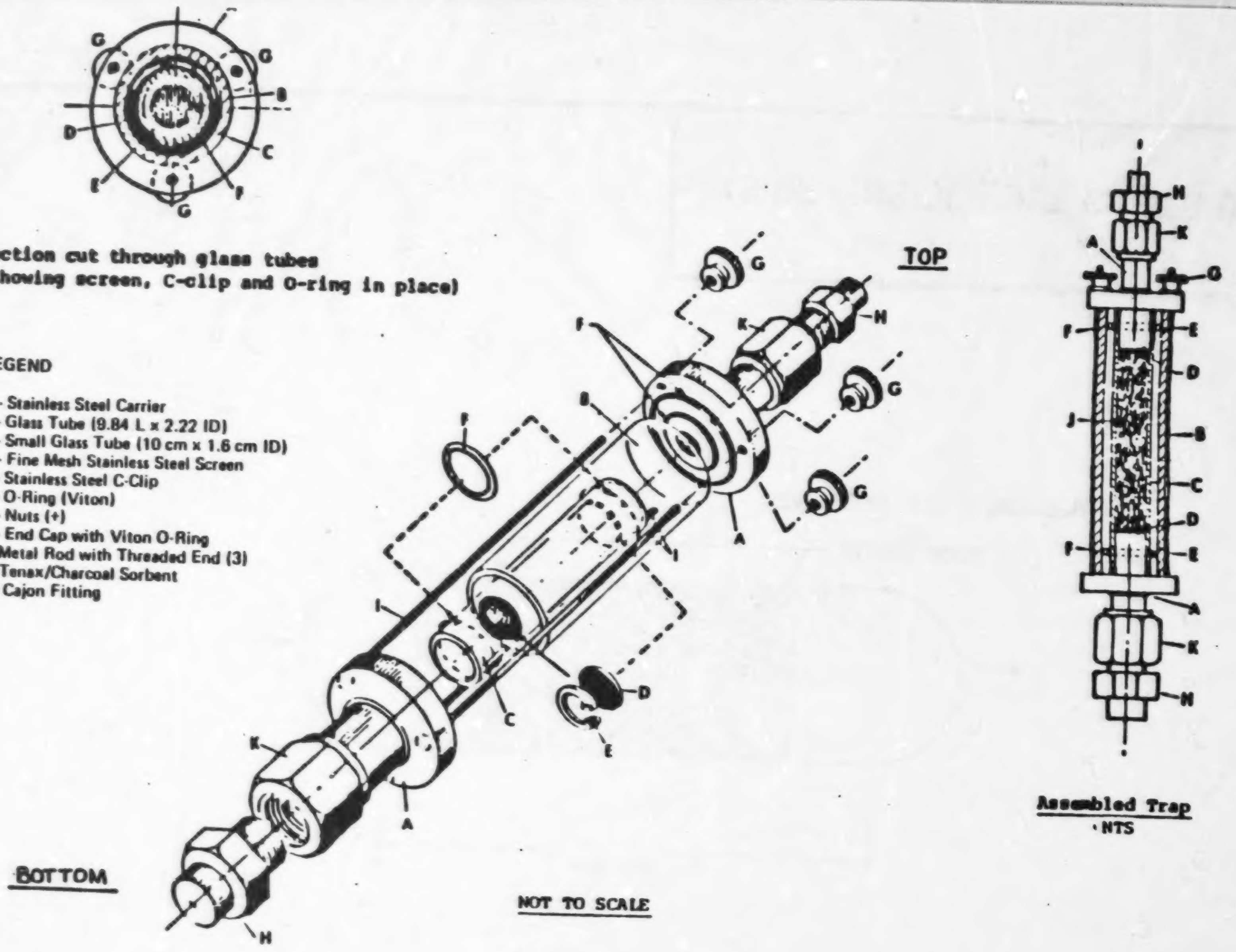

~10cm
~1.6cm
TENAX
GLASSWOOL
OR
STAINLESS STEEL SCREEN

Figure 1.2.1.13 - 3

INSIDE - INSIDE VOST CARTRIDGE


G
G
B
D
C
E
F
G
TOP
G
F
K
H
B
G
F
G
A
I
I
D
C
E
K
A
BOTTOM
H
NOT TO SCALE
H
K
A
G
F
E
D
J
B
C
D
F
E
A
K
H
Assembled Trap
NTS

Section cut through glass tubes
(showing screen, C-clip and O-ring in place)

LEGEND

A - Stainless Steel Carrier
B - Glass Tube (9.84 L x 2.22 ID)
C - Small Glass Tube (10 cm x 1.6 cm ID)
D - Fine Mesh Stainless Steel Screen
E - Stainless Steel C-Clip
F - O-Ring (Viton)
G - Nuts (+)
H - End Cap with Viton O-Ring
I - Metal Rod with Threaded End (3)
J - Tenax/Charcoal Sorbent
K - Cajon Fitting

Figure 1.2.1.13 - 4. Sorbent Trap Assembly (I/O) Volatile Organic Sampling Train (VOST).

2,6-Diphenylene oxide polymer (Tenax, 35/60 mesh)

The new Tenax is Soxhlet extracted for 24 hr with methanol (Burdick & Jackson, pesticide grade or equivalent). The Tenax is dried for 6 hrs in a vacuum oven at 50° C before use. Users of I/O and I/I sorbent cartridges have used slightly different thermal conditioning procedures. I/O sorbent cartridges packed with Tenax are thermally conditioned by flowing organic-free nitrogen (30 milliliters per minute [ml/min]) through the resin while heating to 190° C. Some users have extracted new Tenax and charcoal with pentane to remove non-polar impurities. However, these users have experienced problems with residual pentane in the sorbents during analysis.

If very high concentrations of volatile POHCs have been collected on the resin (e.g., micrograms of analytes), the sorbent may require soxhlet extraction as described above. Previously used Tenax cartridges are thermally reconditioned by the method described above.

Charcoal (SKC Petroleum-Base or Equivalent)

New charcoal is prepared and charcoal is reconditioned as described in the paragraph on 2,6-diphenylene oxide polymer above. Charcoal should be reconditioned by flowing organic-free nitrogen (30 ml/min) through the charcoal while heating to 250° C for 4 hrs. Users of VOST have restricted the types of charcoal used in sorbent cartridges to only petroleum-based types. Criteria for other types of charcoal are acceptable if recovery of POHC in laboratory evaluations meet the criteria of 50 to 150%.

Viton O-Ring

All O-rings used in VOST shall be Viton. Prior to use, these O-rings should be thermally conditioned at 200° C for 48 hours. O-rings should be stored in clean, screw-capped glass containers prior to use.

Glass Tubes/Condensers

The glass resin tubes and condensers should be cleaned with a non-ionic detergent in an ultrasonic bath, rinsed well with organic-free water and dried at 110° C. Resin tubes of the I/O design should be assembled prior to storage as described under Procedure Assembly. Resin tubes of the I/I design can be stored in glass containers with Teflon-lined screw caps. Condensers can be capped with appropriate end caps prior to use.

Metal Parts

The stainless steel carriers, C-clips, end plugs, and screens used in the I/O VOST design are cleaned by ultrasonication in a warm non-ionic detergent solution, rinsed with distilled water, air-dried and heated in a muffle furnace for 2 hr at 400° C.

Silica Gel-Indicating Type, 6-16 Mesh

New silica gel may be used as received. Silica gel which has been previously used should be dried for 2 hr at 175° C.

Crushed Ice

Any commercial source of crushed ice may be used as a coolant for water cooling the condensers.

Water

Water used for leak checking the resin cartridges should be distilled; water used for cooling train components in the field may be tap water; and water used for rinsing glassware should be organic-free.

Glass Wool

Glass wool should be Soxhlet extracted for 8 to 16 hours using pentane and oven dried at 110° C before use. The glass wool should be checked prior to use to ensure that it does not contain residual pentane. If all pentane cannot be removed, an alternate solvent may be used.

Procedure Assembly

The assembly and packing of the sorbent cartridges should be carried out in an area free of volatile organic material. This is preferably done in a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered. Alternatively, the assembly procedures can be conducted in a glove box which can be purged with organic-free nitrogen.

Tenax Cartridges

The Tenax, glass tubes, and metal cartridge parts are cleaned and stored. Approximately 1.6 g of Tenax is weighed and packed into the sorbent tube which has a stainless steel screen and C-clip (I/O design) or glass wool (I/I design) in the downstream end. The Tenax is held in place by inserting a stainless steel screen and C-clips in the upstream end (I/O design) or glass wool (I/I design). The cartridges are then leak checked by putting on one of the end caps and pressurizing them to 30 psi with organic-free nitrogen and immersing the cartridge in distilled water to check for the appearance of bubbles. Cartridges which are determined to be leak-free are then conditioned as described below. (Refer to Tenax/Charcoal Tubes.)

Conditioned resin tubes of the I/O design are then assembled into the metal carriers according to the previously described inside/inside or inside/outside procedures (with end caps) and are placed in ice water for storage and transport. Conditioned resin tubes of the I/I design are capped and placed in ice water for storage and transport.

Tenax/Charcoal Tubes

The Tenax, charcoal, and metal cartridge parts are cleaned and stored as previously described in the Apparatus Section. The tubes are packed with approximately a 3:1 volume ratio of Tenax and Charcoal (approximately 1 g each). The Tenax and Charcoal are held in place by the stainless steel screens and C-clips (I/O design) or by glass wool (I/I design). The glass tubes of the I/O design containing the Tenax and Charcoal are the leak checked (refer to Tenax Cartridge in the Apparatus Section) and conditioned as described in the next section on drop conditioning. Place the I/O glass tubes in the metal carriers as described in the Apparatus Section (refer to Inside/outside type Sorbent Cartridge), put end cap on the assembled cartridge and place the assembled dumps in ice water for storage and transport.

Glass tubes of the I/I design are leak checked, conditioned, and stored in the same manner as the I/O tubes.

Trap Conditioning - QA

Following assembly and leak checking, the traps are connected to a source of organic-free nitrogen and nitrogen is passed through each trap at a flow rate of 30 ml/min, while the traps are heated to 190° C for 4 hr. The effluent from the trap is monitored with a flame ionization detector to check for emission of volatile organic compounds from the trap assembly. The conditioning is continued until no emissions are observed from the trap at the detection limit of the detector. All traps shall be conditioned as above for two separate 4-hr periods.

After conditioning, traps are sealed as discussed in the Apparatus Section (see the I/I or I/O type Sorbent Cartridge Section) and placed under ice water until sampling is accomplished. Conditioned traps should be held for a minimum amount of time to prevent the possibility of contamination.

It may be useful to spike the Tenax and Tenax charcoal traps with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions. After spiked traps are analyzed they may be reconditioned and packed for sampling.

Pretest Preparation

All train components shall be cleaned and assembled as previously described. A dry gas meter shall have been calibrated within 30 days prior to use, using an EPA-supplied standard orifice.

The VOST is assembled according to the schematic diagram in Figure 2. Cooling water should be circulated to the condensers and the temperature of the cooling water should be maintained near 0° C. The end caps of the sorbent cartridges should be placed in a clean screw-capped glass container during sample collection.

Leak Checking

The train is leak checked by closing the valve at the inlet to the first condenser and pulling a vacuum of 250 mm (10 in Hg) above the normal operating pressure. The traps and condensers are isolated from the pump and the leak rate noted. The leak rate should be less than 2.5 mm Hg after 1 min. The train is then returned to atmospheric pressure by attaching a charcoal-filled tube to the train inlet and admitting ambient air filtered through the charcoal. This procedures will minimize contamination of the VOST train components by excessive exposure to the fugitive emissions at hazardous waste incinerator sites.

Sample Collection

After leak checking, sample collection is accomplished by opening the valve at the inlet to the first condenser, turning on the pump and sampling at a rate of 1 liter/min, for 20 min. The volume of sample for any pair of traps should not exceed 20 liters.

Following collection of 20 liters of sample the train is leak checked a second time and the train is returned to atmospheric pressure, using the method discussed in the Assembly Section and the two sorbent cartridges are removed. The end caps are replaced and the cartridges shall be placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specification.

A new pair of cartridges is placed in the VOST, the VOST leak checked and the sample collection process repeated as described above. Sample collection continues until six pairs of traps have been used.

All sample cartridges should be kept in ice water until they are ready for analysis.

Field Blanks/Trip Blanks

Blank Tenax and Tenax charcoal cartridges are taken to the sampling site and the end caps removed for the period of time required to exchange two pairs of traps on VOST. After the two VOST traps have been exchanged, the end caps are replaced on the blank Tenax and Tenax charcoal tubes and these are returned to ice water storage and analyzed with the sample traps. At least one pair of field blanks (one Tenax, one Tenax charcoal) shall be included with each six pairs of sample cartridges collected (or for each field trial using VOST to collect volatile POHCs).

Trip Blanks

At least one pair of blank cartridges (one Tenax, one Tenax charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site. These "field blanks" will be treated as any other cartridges except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination which may occur during storage and shipment.

Laboratory Blanks

One pair of blank cartridges (one Tenax, one Tenax/charcoal) will remain in the laboratory using the method of storage which is used for field samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular POHC), the laboratory blank shall be analyzed in order to identify the source of contamination.

Precision and Accuracy

The results of laboratory evaluations of the VOST for selected POHCs showed that recovery of the analytes from replicate traps ranged from 50 to 150 percent of the expected value.

Prior to field operation of the VOST at a hazardous waste incinerator, a laboratory evaluation of the VOST should be conducted using either selected volatile POHCs of interest or two or more of the volatile POHCs for which data are available. The results of this laboratory evaluation for replicate pairs of traps should demonstrate that recovery of the analytes for replicate pairs of traps fall within the accepted range of performance for these analytes.

1.2.1.20 Bailer

The bailer is one of the oldest and simplest methods available. It consists of a container attached to a cable which is lowered into the well to retrieve a sample. Bailers can be of various designs. The simplest is a weighted bottle or basally-capped length of pipe which fills from the top as it is lowered into the well. More sophisticated bailers have a check valve located at the base which allows water to enter from the bottom as it is lowered into the well. When the bailer is lifted, the check valve closes, allowing water in the bailer to be brought to the surface. More sophisticated bailers are available that remain open at both ends while lowered into the well, but can be sealed at both top and bottom by activating a triggering mechanism from the surface. This allows more reliable sampling at discrete depths within a well. Perhaps the best known bailer of this design is the Kemmerer sampler.

Bailers generally provide an excellent means for collecting samples from monitoring wells. They can be constructed from a wide variety of materials compatible with the parameter of interest. Since they are relatively inexpensive, bailers can be easily dedicated to an individual well to minimize cross contamination during sampling. If not dedicated to a well, they can be easily cleaned to prevent cross contamination. Unfortunately, bailers are frequently not suited for well evacuation because of their small volume (refer to Table 5).

1.2.1.21 Suction Pumps

As the name implies, suction pumps operate by creating a partial vacuum in a sampling tube. This allows the pressure exerted by the atmosphere on the water in the well to force water up the tube to the surface. Accordingly, these pumps are located at the surface and require only that a transmission tube be lowered into the well. Unfortunately, their use is limited by their reliance on suction to depths of 20 to 25 feet, depending on the pump. In addition, their use may result in out gasing of dissolved gases or volatile organics and is therefore limited in many sampling applications. In spite of this, suction methods may provide a suitable means for well evacuation since the water remaining in the well is left reasonably undisturbed.

A variety of pumps are available that operate on this principle, but the most commonly suggested ones for monitoring purposes are the centrifugal and peristaltic pumps. In the centrifugal pump, the fluid is displaced by the action of an impeller rotating inside the pump chamber. This discharges water by centrifugal force. The resulting pressure drop in the chamber creates a suction and causes water to enter the intake pipe in the well. These pumps can provide substantial yields and are readily available and inexpensive. The disadvantages are that they require an external power source and may be difficult to clean between sampling events. In addition the materials with which these pumps are constructed may frequently be incompatible with sampling certain constituents. However, their substantial pumping rates make them suitable for well evacuation.

Peristaltic pumps operate in a similar manner to centrifugal pumps but displace the fluid by mechanical peristalsis. A flexible transmission line is mounted around the perimeter of the pump chamber and rotating rollers compress the tubing, forcing fluid movement ahead (the peristaltic effect) and inducing suction behind each roller. This design isolates the sample from the moving part of the pump and allows for easy cleaning by removal and replacement of the flexible tubing. Unfortunately, peristaltic pumps are generally capable of providing only relatively low yields. They are, therefore, not well suited for well evacuation (refer to Table 5).

1.2.1.22 Positive Displacement Pumps

A variety of positive displacement pumps are available for use in withdrawing water from wells. These methods utilize some pumping mechanism placed in the well that forces water from the bottom of the well to surface by some means of positive displacement. This minimizes the potential for aerating or stripping volatile organics from the sample during removal from the well.

The submersible centrifugal pump is one common example of a positive displacement pump. It works in a similar manner to the centrifugal suction lift pump previously described except the pump and electric motor are lowered into the well. As the impeller rotates and fluid is brought into the pump, fluid is displaced up the transmission line and out of the well. These pumps are capable of providing a high yield. However, they require an external source of power and are frequently constructed with materials and contain lubricants incompatible with sampling certain constituents, particularly organics. They require considerable equipment and effort to move from well to well. Cleaning between sampling events is also difficult, and until recently, they have not been available for well diameters less than 3 inches.

Piston-driven or reciprocating piston pumps are another example of common positive displacement pumps. These pumps consist of a piston in a submerged cylinder operated by a rod connected to the drive mechanism at the surface. A flap valve or ball-check valve is located immediately above or below the piston cylinder. As the piston is lowered in the cylinder, the check valve opens and water fills the chamber. On the upstroke, the check valve closes and water is forced out of the cylinder up into the transmission line and to the surface. The transmission line or piston contains a second check valve that closes on the down stroke, preventing water from re-entering the cylinder. These pumps are capable of providing high yields. However, moving these pumps from well to well is difficult, and their use in monitoring programs may require that a pump be dedicated to each well. Many of these pumps may not be constructed with materials compatible with monitoring certain constituents.

A special adaptation of this pump has recently become available for use in groundwater monitoring. These piston-pumps use compressed gas rather than a rod connected to a driving mechanism at the surface to drive the pistons. This provides a much more convenient and portable means for collecting samples from monitoring wells. They provide good yields and can be constructed with materials compatible to many sampling programs.

Another positive displacement pump applicable for monitoring purposes is the gas operated squeeze pump. This pump was originally developed by R. F. Middleburg of the USGS and consequently is referred to as the Middleburg pump. It consists principally of a collapsible membrane inside a long, rigid housing, compressed gas supply, and appropriate control valves. When the pump is submerged, water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and membrane, forcing the water upward through a sampling tube. When the pressure is released, the top check valve prevents the sample from flowing back down the discharge line, and water from the well again enters the pump through the bottom check valve.

Gas operated squeeze pumps offer a number of advantages for use in groundwater monitoring programs. They can be constructed in diameters as small as one inch and from a wide variety of materials. They are also relatively portable and are capable of providing a fair range of pumping rates. Most importantly, the driving gas does not contact the water sample, thus eliminating possible contamination or gas stripping. However, they do require a gas source, and withdrawal of water from substantial depths may require large gas volumes and long pumping cycles.

Jet pumps are a common submersible pump used in small domestic water wells and may in some cases be suggested for use in monitoring wells. These pumps operate by injecting water through a pipe down into the well. A venturi device is located at the intake portion of the pump. As the water injected from the surface passes through the constricted portion of the venturi, the velocity increases and pressures decrease according to Bennoulli's principle. If the discharge velocity at the nozzle is great enough, the pressure at this point will be lowered sufficiently to draw water into the venturi assembly through the intake and brought to the surface with the original water injected into the well. This additional increment of water is then made available at the surface as the pumps output. Since jet pumps require priming with water and the water taken from the well mixes with water circulating in the system, they are clearly not applicable to collecting samples for monitoring purposes. For similar reasons, their use is not recommended for well evacuation (refer to Table 1.2.1.22).

TABLE 1.2.1.22. ADVANTAGES AND DISADVANTAGES OF MONITORING WELL SAMPLING EQUIPMENT (Larson, 1981a)

Type	Advantages	Disadvantages
A. Bailer	* Can be constructed in a wide variety of diameters * Can be constructed from a wide variety of materials * No external power source required * Extremely portable * Low surface-area-to-volume ratio, resulting in a very small amount of outgassing of volatile organics while sample is contained in bailer * Easy to clean * Readily available * Inexpensive	* Time-consuming sampling; sometimes impractical to properly evacuate casing before taking actual samples * Transfer of water to sample bottle may result in aeration
B. Suction Lift Pump	* Relatively portable * Readily available * Inexpensive	* Sampling is limited to situations where water levels are within about 20 ft from ground surface * Vacuum effect can cause the water to lose some dissolved gas and volatile organics * Frequently not constructed with materials compatible with sampling certain constituents

TABLE 1.2.1.22. (Cont.)

Type	Advantages	Disadvantages
C. Submersible Pumps	* Wide range in diameters * Various material are available * Fairly portable * Depending on size of pump and pumping depths, relatively large pumping rates are possible * Positive displacement minimizes loss of volatiles during pumping * Readily available	* Conventional units are unable to pump sediment-laden water without incurring damage to the pump * Relatively expensive
D. Gas-Operated Squeeze Pump (Middleburg type)	* Can be constructed in diameters as small as 1 inch * Can be constructed from a wide variety of materials * Relatively portable * Fair range in pumping rates is possible * Driving gas does not contact water sample, eliminating possible contamination or gas stripping * Positive displacement minimizes loss of volatiles	* Gas source required * Large gas volumes and long cycles are necessary for deep operation * Pumping rates are not as great as with suction or submersible pumps * Commercial units are relatively expensive - about $2,500 for a fully equipped unit

TABLE 1.2.1.22. (Cont.)

Type	Advantages	Disadvantages
E. Gas-Driven Piston Pump	* Isolates the sample from the operating gas * Requires no electrical power source * Operates continuously and reliably over extended periods of time * Uses compressed gas economically * Can be operated at pumping heads in excess of 500 meters * Positive displacement minimizes loss of volatiles	* Relatively expensive - in excess of $3,000 for the continuously operating unit * Particulate material may damage or inactivate pump unless the suction line is filtered * Low pumping rates
F. Jet Pumps	* Capable of producing high yields * Commonly used in shallow domestic wells * Available for relatively small diameter wells	* Requires priming and mixing sample with water circulating in pump, greatly limiting any use in monitor well applications * Use of venturi may result in stripping of volatiles

1.2.1.30 Pressure-Vacuum Lysimeters

The basic construction of these devices (shown in Figure 1.2.1.30) consists of a porous ceramic cup with a bubbling pressure of 1 bar or greater attached to a short piece of PVC pipe of suitable diameter. Two tubes extend down into the device as illustrated. Data by Silkworth and Grigal (1981) indicate that of the two commercially avialable sampler sizes (2.2 and 4.8 cm diameter), the larger ceramic cup sampler is more reliable, influences water quality less, and yields samples of suitable volume for analysis.

Detailed installation instructions for pressure-vacuum lysimeters are given by Parizek and Lane (1970). Significant modification may be necessary to adapt these instruments to field use where heavy equipment is working. To prevent channelling of contaminated surface water directly to the sampling device, the sampler may be installed in the side wall of an access trench. Since random placement procedures may locate a sampler in the middle of an active area, the sample collection tube should be protected at the surface from heavy equipment by a manhole cover, brightly painted steel cage or other structure. Another problem associated with such sampler placement is that its presence may alter waste management activities (i.e., waste applications, tilling, etc. will avoid the location); therefore, the sampler would not yield representative leachate samples. This problem may be avoided by running the collection tube horizontally underground about 10 m before surfacing.

For sampling after the unit is in place, a vacuum is placed on the system and the tubes are clamped off. Surrounding soil water is drawn into the ceramic cup and up the polyethylene tube. To collect the water sample, the vacuum is released and one tube is placed in a sample container. Air pressure is applied to the other tube which forces the liquid up the tube and into the sample container. Preliminary testing should ensure that waste products can pass into the ceramic cup. If sampling for organics, an inert tubing such as Teflon should be substituted for the polyethylene to prevent organic contamination.

This device is not recommended for volatiles unless a special trap device is used (Hazardous Waste Land Treatment SW-874). The major advantages of these sampling devices are that they are easily available, relatively inexpensive to purchase and install, and quite reliable. The major disadvantage is the potential for water quality alterations due to the ceramic cup, and this possible problem requires further testing. For a given installation, the device chosen should be specifically tested using solutions containing the soluble hazardous constituents of the waste to be land treated.

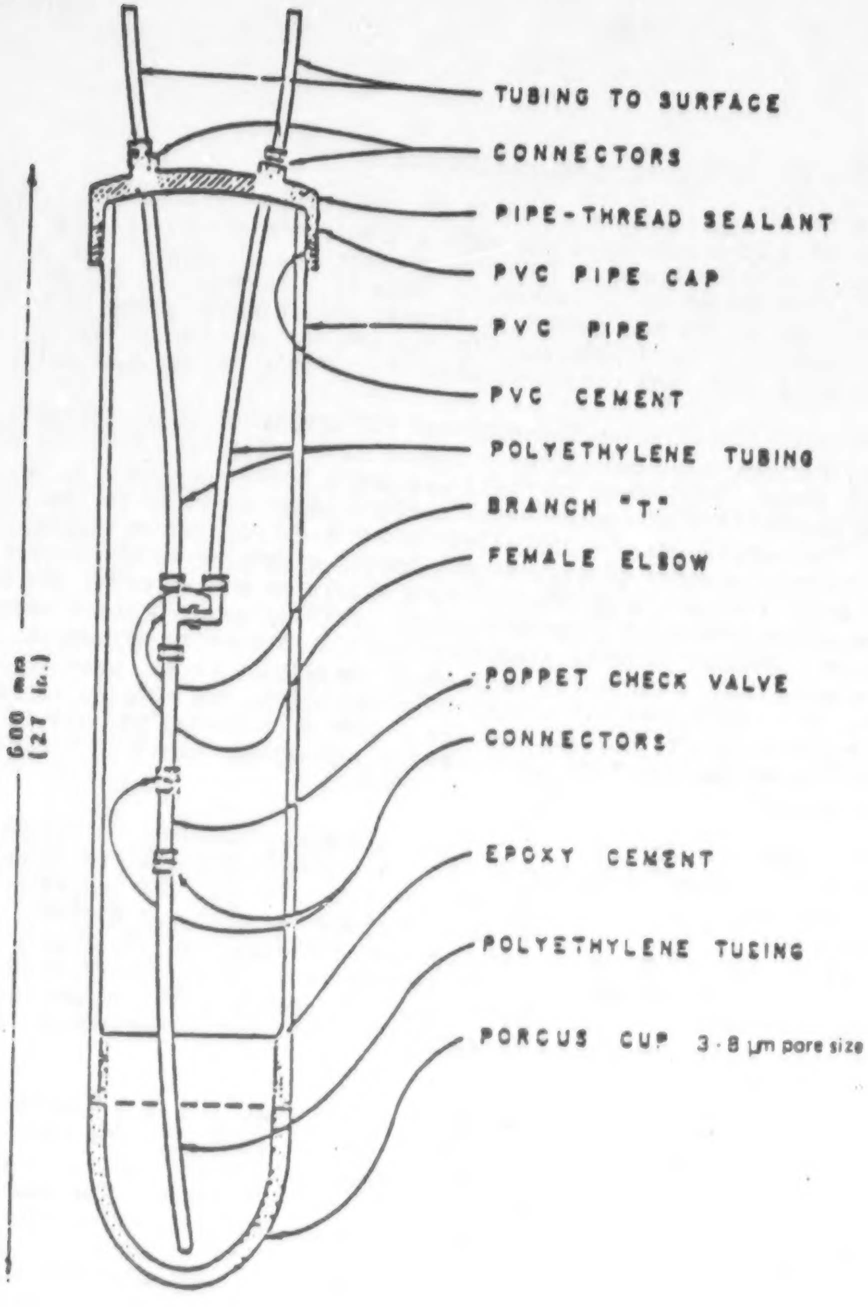

TUBING TO SURFACE
CONNECTORS
PIPE-THREAD SEALANT
PVC PIPE CAP
PVC PIPE
PVC CEMENT
POLYETHYLENE TUBING
BRANCH "T"
FEMALE ELBOW
POPPET CHECK VALVE
CONNECTORS
EPOXY CEMENT
POLYETHYLENE TUBING
PORCUS CUP 3 - 8 μm pore size
600 mm
(27 in.)

Figure 1.2.2.30 One example of a pressure-vacuum lysimeter (Wood, 1973). Reprinted by permission of the American Geophysical Union.

1.2.1.30.1 References

Silkworth, D.R. and D.F. Grigal. 1981. Field comparison of soil solution samplers. Soil Sci. Soc. Am. J. 45:440-442.

Parizek, R.R. and B.E. Lane. 1970. Soil-water sampling using pan and deep pressure-vacuum lysimeters. J. Hydr. 11:1-21.

EPA. 1983. Hazardous Waste Land Treatment. U.S. EPA, Office of Solid Waste and Emergency Response. Washington, DC, SW-874.

Wood, W.W. 1973. A technique using porous cups for water sampling at any depth in the unsaturated zone. Water Resources Research. 9:486-488.

1.2.1.31 Vacuum Extractor

Vacuum extractors were developed by Duke and Haise (1973) to extract moisture from soils above the groundwater table. The basic device consists of a stainless steel trough that contains ceramic tubes packed in soil. The unit is sized not to interfere with ambient soil water potentials (Corey, 1974), and it is installed at a given depth in the soil with a slight slope toward the collection bottle which is in the bottom of an adjacent access hole. The system is evacuated and moisture moved from adjacent soil into the ceramic tubes and into the collection bottle from which it can be withdrawn as desired. The advantage of this system is that it yields a quantitative estimate of leachate flux as well as provides a water sample for analysis. The volume of collected leachate per unit area per unit time is an estimate of the downward movement of leachate water at that depth. The major disadvantages to this system are: it is delicate, requires a trained operator, estimates leachate quantity somewhat lower than actual field drainage, and disturbs the soil above the sampler. Further details about the use of the vacuum extractor are given by Trout et. al. (1975). Performance of this type device is generally poor when installed in clay soils.

1.2.1.31.1 References

Duke, H.R.; and H.R. Haise. 1973. Vacuum Extractors to assess deep percolation losses and chemical constituents of soil water. Soil Sci. Soc. Am. Proc. 37:963-4.

Corey, P.R. 1974. Soil water monitoring. Unpublished report to Dept. of Agr. Eng. Colorado State Univ., Ft. Collins, Colorado.

Trout, T.J., J.L. Smith, & D.B. McWhorter. 1975. Environmental effects of land application of digested municipal sewage sludge. Report submitted to city of Boulder, Colorado, Dept. of Agr. Engr., Colorado State Univ., Ft. Collins, Colorado.

1.2.1.32 Trench Lysimeters

Trench lysimeters get their name from the large access trench or caisson necessary for operation. Basic installation as described by Parizek and Lane (1970) involves excavating a rather large trench and shoring up the side walls, taking care to leave open areas so that samplers can be placed in the side walls. Sample trays are imbedded in the side walls and connected by tubing to sample collection containers. The entire trench area is then covered to prevent flooding. One significant danger in using this system is the potential for accumulation of hazardous fumes in the trench which may endanger the health and safety of the person collecting the samples.

Trench lysimeters function by intercepting downward moving water and diverting it into a collection device located at a lower elevation. Thus, the intercepting agent may be an open-ended pipe, sheet metal trough, pan, or other similar device. Pans 0.9 to 1.2 m in diameter have been successfully used in the field by Tyler and Thomas (1977). Since there is no vacuum applied to the system, only free water in excess of saturation is sampled. Consequently, samples are plentiful during rainy seasons but are nonexistent during the dry season.

Another variation of this system is to use a funnel filled with clean sand inserted into the sidewall of the trench. Freewater will drain into a collection chamber from which a sample is periodically removed by vacuum. A small sample collection device such as this may be preferable to the large trench since the necessary hole is smaller, thus making installation easier (Figure 1.2.1.32)

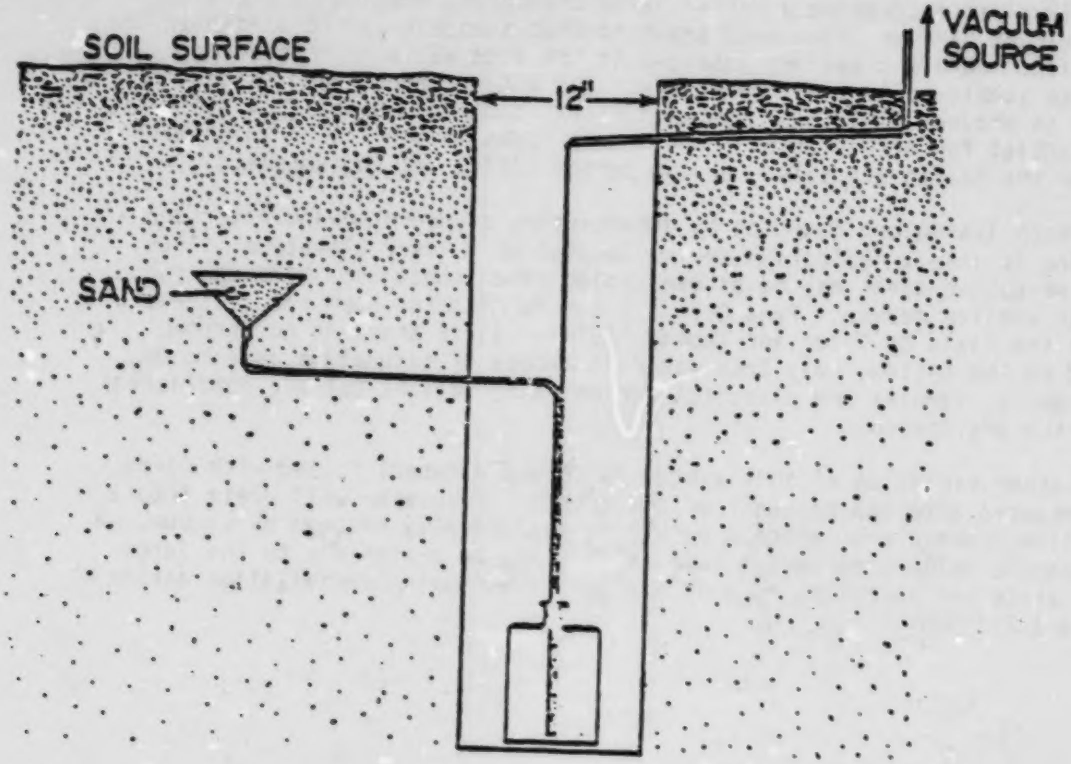

SOIL SURFACE
12"
VACUUM SOURCE
SAND

Figure 1.2.1.32 Schematic diagram of a sand filled funnel used to collect leachate from the unsaturated zone.

1.2.1.32.1 References

Parizek, R.R. and B.E. Lane. 1970. Soil-water sampling using pan and deep pressure-vacuum lysimeters. J. Hydr. 11:1-21.

Tyler, D.D. and G.W. Thomas. 1977. Lysimeter measurements of nitrate and chloride losses and no-tillage corn. J. Environ. Qual. 6:63-66.

1.4.5 Stack Sampling

Owners or operators of hazardous waste facilities that incinerate hazardous wastes are required to demonstrate that the principal organic hazardous constituents (POHCs) in the waste are destroyed at 99.99% efficiency. As part of this demonstration owners or operators will usually need to conduct a trial burn to obtain samples to verify the required destruction and removal efficiency (DRE) for the POHCs. During the trial burn samples of all the effluents are taken and analyzed for POHCs. By knowing the concentrations leaving the incinerator, the facility owner or operator can calculate the DRE.

POHCs in the waste feed are selected on the basis of concentration, toxicity, and difficulty of incineration. POHCs will most likely be selected from compounds or materials on Appendix VIII of 40 CFR Part 261 which contain halogen. (Halogenated compounds and compounds containing phosphorus are frequently toxic and difficult to burn.)

Although there are a number of effluent streams leaving an incinerator, the stream of primary concern will be particulates and gases leaving the stack. Therefore stack sampling plays a critical role in determining whether a given incinerator meets the required 99.99% DRE. Basic sampling trains for stack sampling described in this manual generally parallel EPA methods 1 through 5 in Appendix A of 40 CFR Part 60.

There are currently three accepted methods for sampling stack gases and particulates from hazardous waste incinerators. These methods are the Modified Method 5 (MM5), the Source Assessment Sampling System (SASS), and the Volatile Organics Sampling Train (VOST). Each of these methods are presented in detail in Sections 1.2.1.8, 1.2.1.9, and 1.2.1.13, respectively. These three methods are given in the equipment section of the manual since it is difficult to describe the equipment without discussing its operation at the same time.

Either the MM5 or the SASS sampling methods are acceptable for determining semi- and non-volatile organic components in stack gases and particulates. The VOST method is currently the only method able to determine volatile organics in stack gases at low enough levels with confidence for determining required DREs.

An overview of hazardous waste incineration is presented in Section 3.3 of this manual. Section 3.3 also provides information on sampling and analysis strategies that can be used in the permitting process.

1.4.6 Groundwaters

The methods employed to collect a groundwater sample will be determined by the well characteristics and the parameters which are to be measured. A discussion of the considerations that must be addressed to properly collect a groundwater sample is included in Section 3.1 of this manual. Sections 1.2.1.20 through 1.2.1.22 describe the equipment employed during sampling, while this section discusses the methodology employed when collecting groundwater samples for the analysis of specific parameters.

1.4.6.1 Well Evacuation

While water within the screened portions of a non-pumping well may experience a continued exchange with formation water due to natural flow within an aquifer, limited vertical mixing of water occurs in the casing above the screens. Thus, water standing within a non-pumping well will tend to stratify and stagnate with time. Stagnant water in a monitoring well can develop substantially different chemical characteristics than groundwater in the formation surrounding the well. Changes in the concentration of dissolved gases in the water within the well can occur. This is caused by exchange of gases across the interface between water and the atmosphere within the well. The result can be change in redox conditions and pH in the well. This change can be accompanied by changes in the chemical species present, precipitation or dissolution of metals, and the removal or addition of constituents due to subsequent sorption reactions. The chemical quality of water standing in contact with well materials such as the casing, screen or grouting for long periods of time may also be altered by leaching or adsorption of constituents from those materials. Biological activity within the well may affect certain chemical parameters as well. A common example would be sulfate reducing or iron bacteria that can be responsible for the formation of iron sulfide and iron hydroxide in the well. These compounds may then adsorb selected constituents. Biological activity may also be responsible for the degradation of certain biological constituents.

Consequently, if samples representative of in situ groundwater quality are to be collected during groundwater sampling, the facility permit must specify presampling procedures. These procedures must ensure that stagnant water stored in the monitoring well does not contaminate the sample taken for analysis. Such procedures generally involve prepumping the well prior to sampling to remove or minimize the effect of stagnant water within the well. Several different procedures are available for evacuating stagnant water standing in the well prior to sampling. Their suitability is dependent on a number of site specific factors such as transmissivity of the formation, pumping rate, and well diameter.

1.4.6.1.1 Evacuation to Dryness

The most straightforward procedure for ensuring that stagnant water stored in the well bore will not contaminate samples taken from the well is to remove all the water in the well bore by pumping the well dry. After recovery, the well can be sampled, or preferably, the well can be pumped dry a second time. This ensures that any water surrounding the well that might have been influenced by stagnant well water is removed. After a second recovery, the well can be sampled. In low yielding wells with low recovery rates, pumping the wells dry a second time may prove infeasible due to time constraints. Regardless, complete evacuation of monitoring wells before sampling is the best way to minimize the potential of contaminating the sample with stagnant water stored in the well.

1.4.6.1.2 Removal of Set Volume of Water Prior to Sampling

For wells completed in more permeable formations, however, complete evacuation of the well is frequently not possible with the pumps commonly available for use in monitoring wells or without pumping excessive amounts of water from the formation. In these situations, the traditional practice has been to remove, prior to sampling, an amount of water equal to a set number of the volumes of water equal to that standing in the well. Setting the number of well volumes that are required to be evacuated prior to sampling at an individual well must be based on site specific conditions. The most common procedure for wells screened in moderate to high yield formations, however, has been to pump or bail four to ten times the volume of water standing in the well prior to sampling.

It is not enough for the permit to specify only the volume of water that must be evacuated when specifying evacuation procedures in the facility. The position of the pump intake is critical during well evacuation and should be specified in the permit also. The position of the pump intake during evacuation also significantly affects the locations within the well at which a reliable sample can subsequently be obtained. Consequently, the permit should not only specify the location of the pump intake, but also the location within the well at which samples are to be subsequently taken.

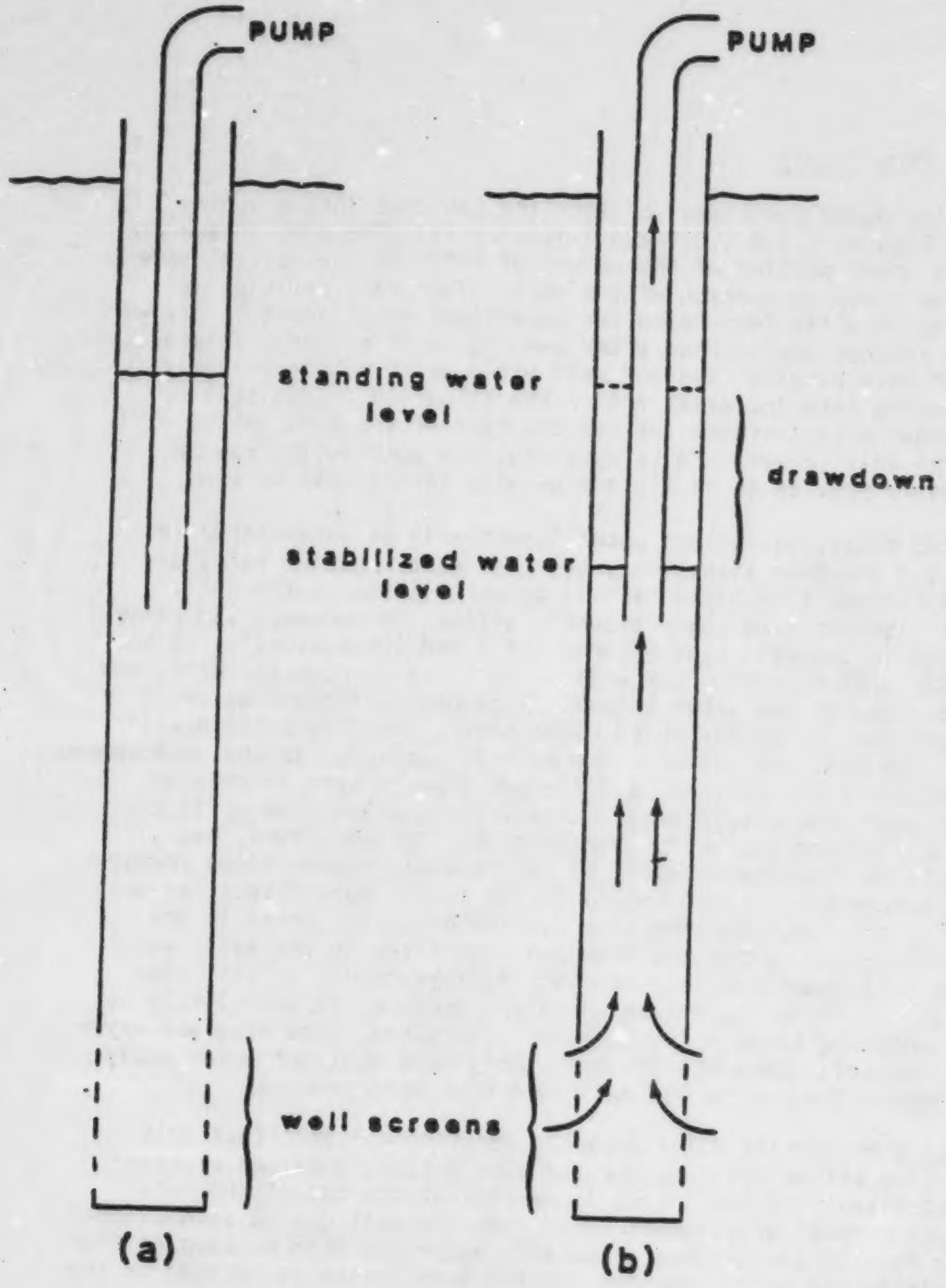
1.4.6.1.3 Pump Intake

There are two basic positions for locating the pump intake during evacuation (see Figures 1.4.5.1.3-1 and 1.4.6.1.3-2). The pump intake can be placed in the upper portion of the column of water in the well at some distance from the screened portion of the well. The exact position is usually specified as a few feet below the waterlevel established in the well as the drawdown reaches equilibrium after pumping is initiated. This position is a function of both pumping rate and well yield or formation transmissivity. Thus, as the pumping rate increases and/or the formation transmissivity decreases, drawdown will increase and the position of the pump intake will move close to the well screens. Alternatively, the pump intake may be located immediately next to or in close proximity to the well screens.

In these two cases, equivalent water levels will be established in the well after the drawdown stabilizes, provided equal pumping rates are utilized, but different flow patterns will be established in the well. These different flow patterns can profoundly affect the exchange and removal of stagnant water in the well (see Figures 1.4.1 and 1.5.6.1.3-1). In the first case, water will flow from the well screens, up through the well, and be removed at the top of the water column. Provided sufficient water is dumped to account for any mixing which might occur, the flow pattern will ensure that all the stagnant water in the well is removed. In the case where the pump is located at the screens, a different flow pattern is created. As pumping is initiated, the water level in the well is drawn down until the water level stabilizes in the well. Before stabilization occurs, two different components of flow are established in the well. Water flows through the well screens from the surrounding formation to the pump intake, as well as from above the screens, removing some portion of water sorted in the casing above the screen. After the drawdown stabilizes in the well, water pumped from the well comes entirely through the formation. At this time, should any water remain in the casing above the screens, it will likely not mix with water entering through the screens. Therefore, some stagnant water will remain in the well above the screens. Only that stagnant water equivalent to the drawdown induced in the well will have been removed.

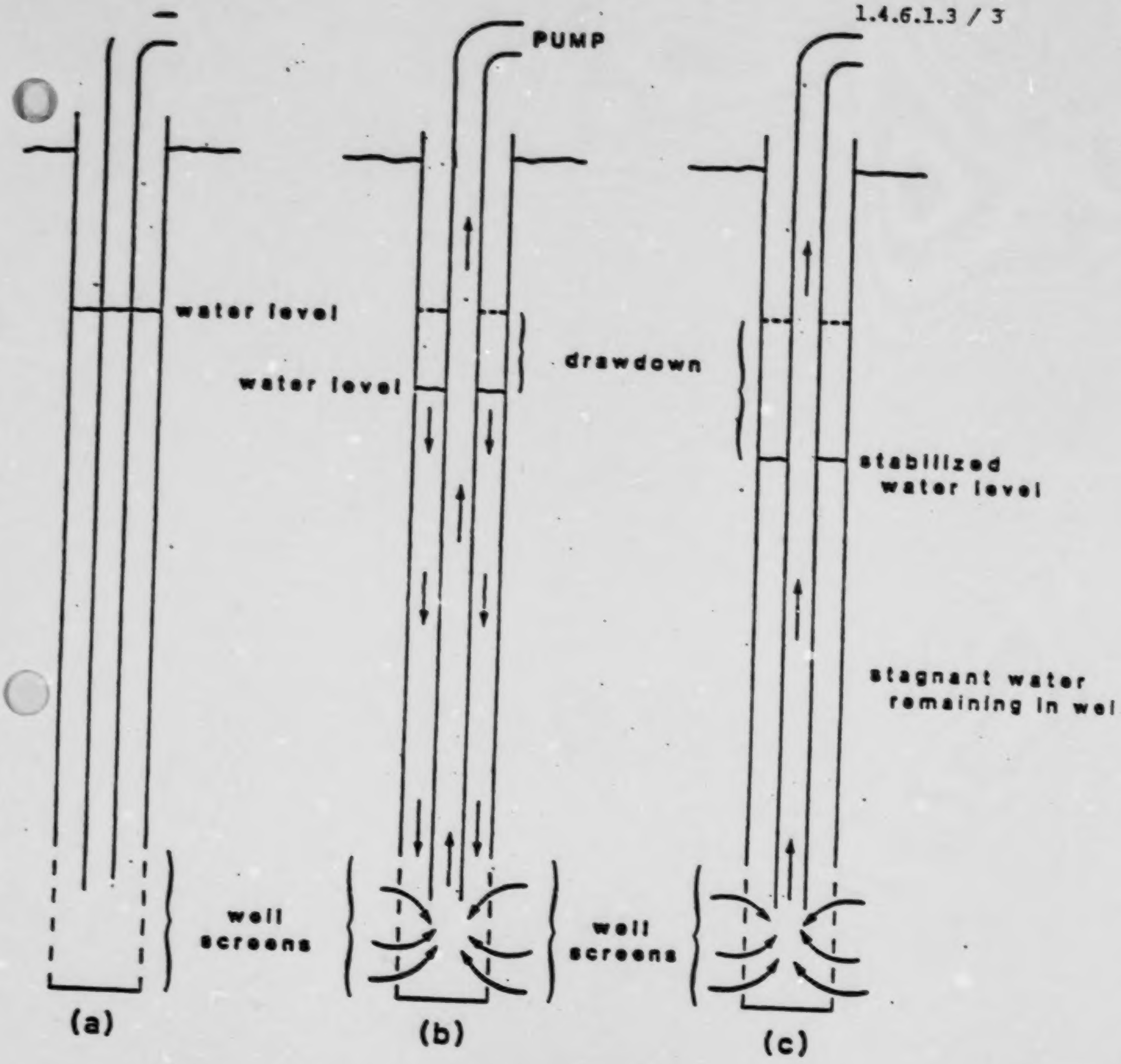
Evacuating monitoring wells prior to sampling can be effectively accomplished using either position for the pump intake, provided certain precautions are taken. If the intake is located at the top of the water column, adequate removal of stagnant water from the well can be accomplished after removing four to six volumes of water. Water can then be sampled from any position within the well. However, if the pump intake is located at the screens, sufficient water must be pumped to stabilize the drawdown in the well, and samples may only be taken at the screen because stagnant water may remain in the well above the casing.

The amount of water that must be evacuated prior to sampling when the pump intake is located at the well screens is highly dependent on the yield of the well. In permeable formations in which the drawdown stabilizes quickly, the necessary prepumping prior to sampling can be substantially less than the recommended 4 to 10 well volumes. In many cases, this reduced amount of prepumping may be advantageous to the monitoring program.


PUMP
PUMP
standing water level
drawdown
stabilized water level
well screens
(a)
(b)

(a) monitoring well prior to evacuation
(b) monitoring well during evacuation with stabilized drawdown

Figure 1.4.1.6.1.3 - 1. Well Evacuation Pump.
Intake located at top of Water Column.


PUMP
water level
water level
drawdown
stabilized
water level
stagnant water
remaining in wel
well
screens
well
screens
(a)
(b)
(c)

(a) monitoring well prior to evacuation
(b) monitoring well during evacuation - drawdown not stabilized and water pumped from casing storage
(c) monitoring well during evacuation - drawdown stabilized and water pumped only from formation

Figure 1.4.1.6.1.3 - 2. Well Evacuation Pump.
Intake located at screens.

1.4.6.1.4 Calculation of the Amount of Water to be Evacuated

Removal of four to ten times the volume of water standing in the well can represent excessively large amounts of water, particularly in wells screened at significant depths below the water table. Prepumping such large amounts of water may unnecessarily lengthen the time required for sampling, making the procedure unnecessarily expensive. In addition, the large amount of water withdrawn during such an evacuation program may require expensive disposal procedures, particularly if it contains significant concentrations of hazardous constitutents. More importantly, excessive prepumping can result in water samples whose quality is not representative of water in the immediate vicinity of the well. This can occur because water from increasingly greater lateral distances from the well intake will be drawn to the well for sampling as the sphere of influence increases with pumpage. This water may be of substantially different quality than that in the immediate vicinity of the monitoring well. In addition, as the theory of partially penetrating wells predicts, vertical components of the flow into the well will also increase with increasing pumpage, thereby drawing water into the sample from strata located either above or below the formation of interest. The development of strong vertical gradients mya also cause the occurrence of flow in the annular space of the well.

At wells in which the pump intake is located next to the screens, the amount of prepumping necessary to ensure that the sample represents water taken from the formation and not from storage in the well is dependent on the well diameter, pumping rate, and aquifer transmissivity or well yield. Gibb and Schuller have presented a method of analysis that provides a basis for specifying adequate prepumping amounts based on these factors. The basis of this analysis is a solution presented by Papadopulos and Cooper, which describes the discharge from a pumped well, accounting not only for the water removed from storage in the aquifer, but also the water removed from storage within the well. Drawdown calculated from this solution differs significantly from that calculated by the Jacob and Theis solutions during the early periods of pumping when the well bore contributes substantial amounts of water. As the pumping approaches equilibrium, water drawn from storage within the well progressively decreases, and the predicted drawdown approaches that predicted by Jacob and Theis solutions.

This solution can also be used to develop an equation that can predict the percentage of water drawn from the aquifer as pumping progresses for specific pumping rates, casing diameters, and formation transmissivities. In Figure 1.4.6.1.4, curves calculated from this equation are presented and show the effect of different transmissivities on the amount of water drawn from the aquifer as pumping progresses for a two-inch diameter well pumping at 500 ml/min. As may be seen for formations of high transmissivity, the percentage of water contributed from well storage reduces rapidly. These curves demonstrate that in highly transmissive formations only a very small amount of pumpage, conceivably less than one well volume, may be required before the contribution from the well storage is negligible and presumably before representative water samples can be obtained.

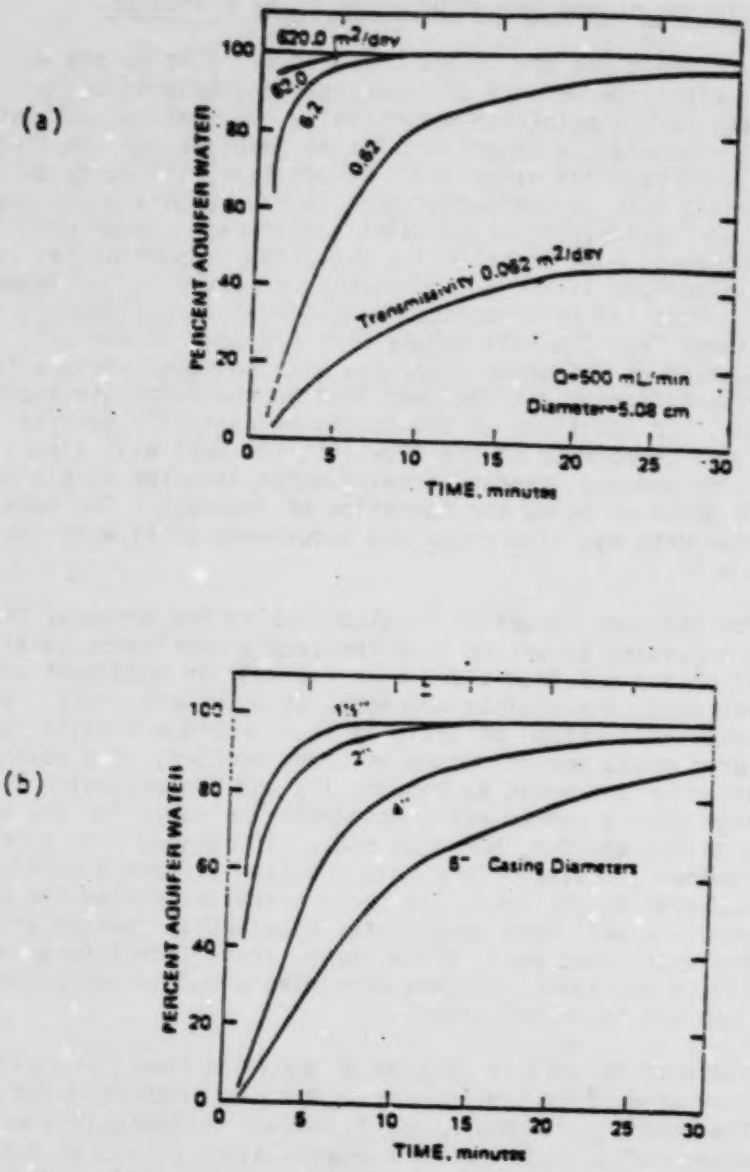


Figure 1.4.6.1.4. Percent of Aquifer Water Withdrawn Versus Time: (a) for various transim transmissivities and (b) various well casing diameters (from Gibbs et al., 1981).

Similar curves depicting the percentage of water drawn from a formation of known transmissivity as pumping progresses can be developed for wells of various diameters using different pumping rates (see, for example, Figure 3). These may be used by the applicant to provide a basis for establishing prepumping requirements in wells in which the pumps are located next to the screens. The transmissivity values used in this manner may be based on estimates from field or laboratory data. Methods for field and laboratory estimation of hydraulic parameters, such as transmissivity are described in standard texts.

1.4.6.2 Sample Withdrawal

1.4.6.2.1 Introduction

The permit will specify methods for sample withdrawal that ensure that the sample is not altered or contaminated during withdrawal from the well. the sampling equipment must be comprised of materials compatible with the goals of the particular monitoring program. These materials must neither leach nor absorb constituents of interest at levels which might be considered significant. Similarly, sampling equipment must be capable of being disassembled and fully cleaned between sampling events. Methods which allow excessive exposure to the atmosphere or other gases should be avoided when they might influence the measurement of specific constituents. Exposure of the sample to the atmosphere or other gases may result in changes in the concentration of dissolved gases in the sample. As documented by Gibb, et. al., these changes can alter the pH of the sample, which in turn may result in the precipitation or dissolution of specific constituents, particularly metals, and influence water quality measurements. Similarly, changes in the redox potential and, consequently, in the chemical species present, may result. Exposure of the sample to the atmosphere or reduced pressures may also result in the degassing and loss of volatile organics from the sample.

When specifying methods for removal of water from monitoring wells, the permit writer should have examined the proposed methods to ensure that they are suitable both for sample collection and well excavation prior to sampling. In general, evacuation methods require greater pumping rates (see previous section), while sample collection methods emphasize to a greater extent the preservation of sample integrity. In many instances, one method will be suitable for both purposes. However, in some cases the use of different methods for well evacuation and sample collection may be appropriate, and the permit should specify both methods in the facility permit. When examining methods used solely for well evacuation, the permit should not allow the use of any method that might contaminate or otherwise alter the quality of water remaining in the well. Such an alteration would prevent the subsequent removal of samples representative of groundwater quality.

1.4.6.2.2 Pumping

A variety of methods are available for sampling and well evacuation, including bailers, suction lift pumps such as the centrifugal and peristaltic pumps; gas lift methods; and positive displacement or submersible pumps such as centrifugal, piston, gas squeeze, or jet pumps. These methods utilize different principles for operation and have distinct and frequently different advantages and disadvantages when applied to sampling and well evacuation. Each is discussed individually and a summary of their advantages and disadvantages is provided in Sections 1.2.1.20 to 1.2.1.22. Frequently, several methods will be available that can provide a suitable means for well evacuation and sample collection in a particular monitoring program. In such cases, the choice of method will be based partly on such factors as monitoring well diameter, water level, pumping volume, and rate requirements, accessibility of the site, ease of use, and cost. All of these factors are legitimate and should be considered as long as they do not unduly compromise the goals of the sample program.

1.4.6.2.3 Sample Preservation and Shipment

Many of the constituents and parameters that require monitoring in Subpart F programs are not stable and, therefore, sample preservation is very important. Measurement of these parameters may be significantly influenced by changes in the chemical quality of the sample which may occur during periods of shipping and storage prior to analysis. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Certain constituents may also adsorb onto or leach from container surfaces such as glass, plastic, quartz, etc. Certain gaseous constitutents may diffuse through the container wall and be lost from the sample. Biological changes may take place in a sample that can change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution.

To minimize changes in the chemical quality of a sample during shipping and storage prior to analysis, the permit should specify the use of proper containers and adequate procedures for sample preservation and shipment. In many programs, the permit will require the splitting of the sample into several different samples, specifying the different sample containers and preservation methods for each sample based on the analytes of interest. Specific directions on sample preservation are provided in the analysis methods. Table 1.4.6.2.3 outlines appropriate preservation techniques for groundwater samples.

TABLE 1.4.6.2.3. SUMMARY OF SAMPLE PRESERVATION METHODS

Preservative	Action	Applicable to
$HgCl_2$	Bacterial inhibitor	Nitrogen forms, phosphorus forms
Acid (HNO_3)	Metals solvent, prevents precipitation	Metals
Acid (H_2SO_4)	Bacterial inhibitor	Organic samples (COD, oil & grease, organic carbon)
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration	Bacterial inhibitor	Acidity-Alkalinity, organic materials, BOD, color, odor, organic N, carbon, etc., biological organism (coliform, etc.)

Sample containers are discussed in Section 1.2.2 of this manual. The analyst is referred to that section for choice of containers for parameters of interest.

1.4.6.2.4 Filtration

Filtration of samples in which volatile organic constituents are of interest is forbidden since filtration may strip these constituents from the sample. However, filtration of samples in which metals are the constituents of concern may be applicable depending on the proposed analytical method. If total recoverable methods are to be used, the sample should not be filtered. However, if measurement of dissolved metals is desired, the sample may be filtered on site. If filtration is required, the use of a 0.45 micron filter is generally considered appropriate. Although some controversy has existed over the appropriate pore size of the filter due to the relative sizes of clay and colloidal particles, recent studies by Gibb, et. al., have indicated that differences in chemical composition resulting from the use of smaller pore size filters (0.22 microns) are not significant. Thus, the standard 0.45-micron filter still provides a satisfactory and more practical means of sample filtering.

1.4.6.2.5 Chain of Custody

Chain of custody, procedures field logs, sample labels, etc. as provided in this manual should be used for all groundwater sampling episodes. Refer to Section 1.3 for appropriate procedures and guidance.

1.4.7 Land Treatment Sampling

1.4.7.1 Unsaturated Zone Monitoring

The unsaturated zone is described as the layer of soil or parent material separating the bottom of the treatment zone and the seasonal high water table or groundwater table and is usually found to have a moisture content less than saturation. In this zone, the movement of moisture may often be relatively slow in response to soil properties and prevailing climatic conditions; however, in some locations, soils and waste management practices may lead to periods of heavy hydraulic loading which could cause rapid downward flux of moisture.

An unsaturated zone monitoring plan should be developed for two purposes: 1) to detect any significant movement of hazardous constituents out of the system and 2) to furnish information for management decisions. In light of the variability in soil water flux and the mobility of hazardous waste constituents, the unsaturated zone monitoring plan should include sampling the soil to evaluate relatively slow moving waste constituents (soil core monitoring) and sampling the soil-pore liquid to evaluate rapidly moving waste constituents. Monitoring for hazardous constituents should be performed on a representative background plot(s) until background levels are established and immediately below the treatment zone (active portion). The number, location, and depth of soil core and soil-pore liquid samples taken must allow an accurate indication of the quality of soil-pore liquid and soil below the treatment zone and in the background area. The frequency and timing of soil-pore liquid sampling must be based on the frequency, time and rate of waste application, proximity of the treatment zone to groundwater, soil permeability, and amount of precipitation. The data from this program must be sufficient to determine if statistically significant increases in hazardous constituents, or selected indicator constituents have occurred below the treatment zone. Location and depth of soil core and soil-pore liquid samples follow the same reasoning, but the number, frequency and timing of soil core sampling differs somewhat from that required for soil-pore liquid sampling. Thus, the unique aspects of these topics will be considered together with discussions of techniques for obtaining the two types of samples.

1.4.7.1.1 Locating Unsaturated Zone Samples

Soil characteristics, waste type, and waste application rate are all important factors in determining the environmental impact of a particular land treatment unit or part of a unit on the environment. Therefore, areas of the land treatment unit for which these characteristics are similar (i.e., uniform areas) should be sampled as a single monitoring unit. As will be used in further discussions, a uniform area is defined as an area of the active portion of a land treatment unit which is composed of soils of the same soil series (USDA, 1975) and to which similar wastes or waste mixtures are applied at similar application rates. If, however, the texture of the surface soil differs significantly among soils of the same series classification, the phase classification of the soil should be considered in defining "uniform areas." A certified professional soil scientist should be consulted in designating uniform areas.

Based on the above definition, it is recommended that the location of soil core sampling or soil-pore liquid monitoring devices within a given uniform area be randomly selected. Random selection of samples ensures a more accurate representation of conditions within a given uniform area. It is convenient to spot the field location for soil-coring and soil-pore liquid devices by selecting random distances on a coordinate system and using the intersection of the two random distances as the location at which a soil core should be taken or a soil-pore liquid monitoring device installed. This system works well for fields of both regular and irregular shape, since the points outside the area of interest are merely discarded, and only the points inside the area are used in the sample.

The location, within a given uniform area of a land treatment unit (i.e., active portion monitoring), at which a solid core should be taken or a soil-pore liquid monitoring device installed should be determined using the following procedure:

(1) Divide the land treatment unit into uniform areas under the direction of a certified professional soil scientist.

(2) Set up coordinates for each uniform area by establishing two base lines at right angles to each other which intersect at an arbitrarily selected origin, for example, the southwest corner. Each baseline should extend far enough for all of the uniform area to fall within the quadrant.

(3) Establish a scale interval along each base line. The units of this scale may be feet, yards, meters, or other units depending on the size of the uniform area, but both base lines should have the same units.

(4) Draw two random numbers from a random numbers table (usually available in any basic statistics book). Use these numbers to locate one point along each of the base lines.

(5) Locate the intersection of two lines drawn perpendicular to the base lines through these points. This intersection represents one randomly selected location for collection of one soil core, or for installation of one soil-pore liquid device. If this location at the intersection is outside the uniform area, disregard and repeat the above procedure.

(6) For soil-core monitoring, repeat the above procedure as many times as necessary to obtain the desired number of locations within each uniform area of the land treatment unit. This procedure for randomly selecting locations must be repeated for each soil core sampling event but will be needed only once in locating soil pore liquid monitoring devices.

Locations for monitoring on background areas should also be randomly determined. Again, consult a certified professional soil scientist in determining an acceptable background area. The background area must have characteristics (i.e., at least soil series classification) similar to those present in the uniform area of the land treatment unit it is representing, but it should be free from possible contamination from past or present activities which could have contributed to the concentrations of the hazardous constituents of concern. Establish coordinates for an arbitrarily selected portion of the background area and use the above procedure for randomly choosing sampling locations.

1.4.7.1.2 Depth to be Sampled

Since unsaturated zone monitoring is intended to detect pollutant migration from the treatment zone, samples should logically be obtained from immediately below this zone. Care should be taken to assure that samples from active areas of the land treatment unit and background samples are monitoring similar horizons or layers of parent material. Noting that soils seldom consists of smooth, horizontal layers but are often undulating, sloped and sometimes discontinuous, it would be unwise to specify a single depth below the land surface to be used for comparative sampling. A convenient method for choosing sampling depths is to define the bottom of the treatment zone as the bottom of a chosen diagnostic solid horizon and not in terms of a rigid depth. Sampling depth would then be easily defined with respect to the bottom of the treatment zone. At a minimum, soil core and soil-pore liquid sampling should monitor within 30 cm (12 in) of the bottom of the treatment zone. Additional sampling depths may be desirable, for instance if analytical results are inconclusive or questionable. Core samples should include only the 0 to 15 cm increment below the treatment zone while soil-pore liquid samplers should be placed so that they collect liquid from anywhere within this 30 cm zone.

1.4.7.2 Soil Core Sampling Technique

Waste constituents may move slowly through the soil profile for a number of reasons, such as the lack of sufficient soil moisture to leach through the system, a natural or artificially occurring layer or horizon of low hydraulic conductivity, or waste constituents which exhibit only a low to moderate mobility relative to water in soil. Any one or a combination of these effects can be observed by soil core monitoring. Based on the treatment zone concept, only the portions of soil cores collected below the treatment zone need to be analyzed. The intent is to demonstrate whether significantly higher concentrations of hazardous constituents are present and moving in material below the treatment zone than in background soils or parent material.

Soil core sampling should proceed according to a definite plan with regard to number, frequency and technique. Previous discussions of statistical considerations should provide guidance in choosing the number of samples required. Background values for soil core monitoring should be established by collecting at least eight randomly selected soil cores for each soil series present in the treatment zone. These samples can be composited in pairs (from immediately adjacent locations) to form four samples for analysis. For each soil series a background arithmetic mean and variance should be calculated for each hazardous constituent. For monitoring the active portion of the Land Treatment Facility, a minimum of six randomly selected soil cores should be obtained per uniform area and composited as before to yield three samples for analysis. If, however, a uniform area is greater than 5 ha (12 ac), at least two randomly selected soil cores should be taken per 1.5 ha (4 ac) and composited in pairs based on location. Data from the samples in a given uniform area should be averaged and statistically compared. If analyses reveal a large variance from samples within a given uniform area, more samples may be necessary. The frequency with which soil coring should be done is at least semiannually, except for background sampling which, after background values are established, may be performed as needed to verify whether background levels are changing over time.

It is important to keep an accurate record of the locations from which soil core samples have been taken. Even where areas have been judged to be uniform, the best attempts at homogeneous waste application and management cannot achieve perfect uniformity. It is probable in many systems that small problem areas or "hot spots" may occur which cause localized real or apparent pollutant migration. Examples of "apparent" migration might include small areas where waste was applied too heavily or where the machinery on-site mixed waste too deeply. The sampling procedure itself is subject to error and so may indicate apparent pollutant migration. Therefore, anomalous data points can and should be resampled at the suspect location(s) to determine if a problem exists, even if the uniform area as a whole shows no statistically significant pollutant migration.

The methods used for soil sampling are variable and depend partially on the size and depth of the sample needed and the number and frequency of samples to be taken. Of the available equipment, oakfield augers are useful if small samples need to be taken by hand while bucket augers give larger samples. Powered coring or drilling equipment, if available, is the preferable choice since it can rapidly sample to the desired depths and provide a clean, minimally disturbed sample for analysis. Due to the time involved in coring to 1.5 m and sometimes farther, powered equipment can often be less costly than hand sampling. In any case, extreme care must be taken to prevent cross contamination of samples. Loose soil or waste should be scraped away from the surface to prevent it from contaminating samples collected from lower layers. The material removed from the treatment zone portion of the borehole can be analyzed if desired, to evaluate conditions in the treatment zone. It is advisable to record field observations of the treatment zone even if no analysis is done. Finally, bore holes absolutely must be backfilled carefully to prevent hazardous constituents from channelling down the hole. Native soil compacted to about field bulk density, clay slurry or other suitable plug material may be used.

Sample handling, preservation and shipment should follow a chain of custody procedure and a defined preservation method such as is found in Sec. 1 of this document or in the analytical section of EPA document SW-874, Hazardous Waste Land Treatment (1983). If more sample is collected than is needed for analysis, the volume should be reduced by either the quartering or riffle technique. (A riffle is a sample splitting device designed for use with dried ground samples).

The analysis of soild cores must include all hazardous constituents which are reasonably expected to leach or the principal hazardous constituents (PHCs) which generally indicate hazardous constituent movement (EPA, 1982).

1.4.7.3 Soil-Pore Liquid Sampling Technique

Percolating water added to the soil by precipitation, irrigation, or waste applications may pass through the treatment zone and may rapidly transport some mobile waste constituents or degradation products through the unsaturated zone to the groundwater. Soil-pore liquid monitoring is intended to detect these rapid pulses of contaminants, often immediately after heavy precipitation events, that are not likely to be observed through the regularly scheduled analysis of soil cores. Therefore, the timing of soil-pore liquid sampling is a key to the usefulness of this technique. Seasonability is the rule with soil-pore liquid sample timing (i.e., scheduled sampling cannot be on a preset date, but must be geared to precipitation events). Assuming that sampling is done soon after leachate-generating precipitation or snowmelt, the frequency also varies depending on site conditions. As a starting point, sampling should be done quarterly. More frequent sampling may be necessary, for example, at units located in areas with highly permeable soils or high rainfall, or at which wastes are applied very frequently. The timing of sampling should be geared to the waste application schedule as much as possible.

Land treatment units at which wastes are applied infrequently (i.e., only once or twice a year) or where leachate-generating precipitation is highly seasonal, quarterly sampling and analysis of soil-pore liquid may be unnecessary. Because soil-pore liquid is instituted primarily to detect fast-moving hazardous constituents, monitoring for these constituents many months after waste application may be useless. If fast-moving hazardous constituents are to migrate out of the treatment zone, they will usually migrate at least within 90 days following waste application, unless little precipitation or snowmelt has occurred. Therefore, where wastes are applied infrequently or leachate generation is seasonal, soil-pore liquid may be monitored less frequently (semi-annually or annually). A final note about timing is that samples should be obtained as soon as liquid is present. Following any significant rainfall, snowmelt or waste application, the owner or operator should check the monitoring devices for liquid at least within 24 hours.

The background concentrations of hazardous constituents in the soil-pore liquid should be established by installing two monitoring devices at random locations for each soil series present in the treatment zone. Samples should be taken on at least a quarterly basis for at least one year and can be composited to give one sample per quarter. Analysis of these samples should be used to calculate an arithmetic mean and variance for each hazardous constituent. After background values are established, additional soil-pore liquid samples should occasionally be taken to determine if the background values are changing over time.

The number of soil-pore liquid samplers needed is a function of site factors that influence the variability of leachate quality. Active, uniform areas should receive, in the beginning, a minimum of six samplers per uniform area. For uniform areas greater than 5 ha, at least two samplers per 1.5 ha should be installed. Samples may be composited in pairs based on location to give three samples for analysis. The number of devices may have to be adjusted up (or down) as a function of the variability of results.

To date, most leachate collection has been conducted by scientists and researchers and there is not an abundance of available field equipment and techniques. The EPA (1977) and Wilson (1980) have prepared reviews of pressure vacuum lysimeters and trench lysimeters. The pressure vacuum lysimeters are much better adapted to field use and have been used to monitor pollution from various sources (Manbeck, 1975; Nassau-Suffolk Research Task Group, 1969; The Resources Agency of California, 1963; James, 1974). These pressure vacuum samplers are readily available commercially and are the most widely used, both for agricultural and waste monitoring uses. A third type of leachate sampler is the vacuum extractor as used in the field by Smith et al. (1977). A comparison of in situ extractors was presented by Levin and Jackson (1977).

Acceptable soil pore liquid sampling devices are described in Sections 1.2.1.30 to 1.2.1.32 of this manual.

1.4.8 References

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SECTION THREE

MONITORING

3.1 Groundwater

3.1.1 Background

The Environmental Protection Agency has established regulations in 40 CFR Part 264, Subpart F which require owners or operators of hazardous waste facilities to monitor the groundwater beneath their facilities. The purpose of this monitoring is to identify whether the facility is leaking and thus contaminating the groundwater. EPA, through its regulations, has established a simple rule which may be stated as follows:

> The quality of the groundwater beneath a hazardous waste facility must not be adversely affected by the presence of the facility.

In order to determine if the groundwater beneath a facility has been affected, all measurements are referenced to background values. These background values are obtained upgradient from the facility (i.e., groundwater before it flows under the facility), in most cases.

Groundwater monitoring is divided into two phases. The first phase involves testing the groundwater for a few parameters which are indicative of contamination and statistically evaluating whether contamination has occurred. A statistical test is applied to the upgradient versus the downgradient values for each indicator parameter to determine if the facility is leaking. See Section 1.1.5 of this manual. If one or more of the indicator parameters is significantly different from background, the owner or operator must perform the second phase of testing.

The second phase of testing directs the owner or operator to determine the presence of all of the compounds listed on Appendix VIII of Part 261. After compounds from Appendix VIII are found, the owner or operator must quantitate each one and submit the results to the Regional Administrator in an application for a permit modification.

There are presently 375 compounds listed on Appendix VIII and if they are tested for individually, analytical costs may be quite high. This manual provides not only a number of methods suitable for the determination of Appendix VIII compounds in groundwater but also an overall screening method which will allow owners and operators to comply with testing requirements without overtaxing their available analytical resources. For example, all compounds which contain a given element can be screened for by simply determining the total amount of that element present. Using this approach a single determination of lead will allow the owner or operator to establish that lead acetate, lead subacetate, lead phosphate, and other lead compounds are not present. This approach is less resource-intensive yet still provides the groundwater protection required.

3.1.2 Regulatory Definitions

§264.97 General Groundwater Monitoring Requirements

The owner or operator must comply with the following requirements for any groundwater monitoring program developed to satisfy §264.98, §264.99, or §264.100.

(a) The groundwater monitoring system must consist of a sufficient number of wells, installed at appropriate locations and depths to yield groundwater samples from the uppermost aquifer that:

(1) Represent the quality of background water that has not been affected by leakage from a regulated unit; and

(2) Represent the quality of groundwater passing the point of compliance.

(b) If a facility contains more than one regulated unit, separate groundwater monitoring systems are not required for each regulated unit provided that provisions for sampling the groundwater in the uppermost aquifer will enable detection and measurement at the compliance point of hazardous constituents from the regulated units that have entered the groundwater in the uppermost aquifer.

(c) All monitoring wells must be cased in a manner that maintains the integrity of the monitoring-well bore hole. This casing must be screened or perforated and packed with gravel or sand, where necessary, to enable collection of groundwater samples. The annular space (i.e., the space between the bore hole and well casing) above the sampling depth must be sealed to prevent contamination of samples and the groundwater.

(d) The groundwater monitoring program must include consistent sampling and analysis procedures that are designed to ensure monitoring results that provide a reliable indication of groundwater quality below the waste management area. At a minimum the program must include procedures and techniques for:

(1) Sample collection;

(2) Sample preservation and shipment;

(3) Analytical procedures; and

(4) Chain-of-custody control.

(e) The groundwater monitoring program must include sampling and analytical methods that are appropriate for groundwater sampling and that accurately measure hazardous constituents in groundwater samples.

(f) The groundwater monitoring program must include a determination of the groundwater surface elevation each time groundwater is sampled.

(g) Where appropriate, the groundwater monitoring program must establish background groundwater quality for each of the hazardous constituents or monitoring parameters or constituents specified in the permit.

(1) In the detection monitoring program under §264.98, background groundwater quality for a monitoring parameter or constituent must be based on data from quarterly sampling of wells upgradient from the waste management area for one year.

(2) In the compliance monitoring program under §264.98, background groundwater quality for a hazardous constituent must be based on data from upgradient wells that:

(i) Is available before the permit is issued;

(ii) Accounts for measurement errors in sampling and analysis; and

(iii) Accounts, to the extent feasible, for seasonal fluctuations in background groundwater quality if such fluctuations are expected to affect the concentration of the hazardous constituent.

(3) Background quality may be based on sampling of wells that are not upgradient from the waste management area where:

(i) Hydrogeologic conditions do not allow the owner or operator to determine what wells are upgradient; or

(ii) Sampling at other wells will provide an indication of background groundwater quality that is as representative or more representative than that provided by the upgradient wells.

(4) In developing the data base used to determine a background value for each parameter or constituent, the owner or operator must take a minimum of one sample from each well and a minimum of four samples from the entire system used to determine background groundwater quality, each time the system is sampled.

(h) The owner or operator must use the following statistical procedure in determining whether background values or concentration limits have been exceeded:

(1) If, in a detection monitoring program, the level of a constituent at the compliance point is to be compared to the constituent's background value and that background value has a sample coefficient of variation less than 1.00:

(i) The owner or operator must take at least four portions from a sample at each well at the compliance point and determine whether the difference between the mean of the constituent at each well (using all portions taken) and the background value for the constituent is significant at the 0.05 level using the Cochran's Approximation to the Behren-Fisher Student's t-test. If the test indicates that the difference is significant, the owner or operator must repeat the same procedure (with at least the same number of portions as used in the first test) with a fresh sample from the monitoring well. If this second round of analyses indicates that the difference is significant, the owner or operator must conclude that a statistically significant change has occurred; or

(ii) The owner or operator may use an equivalent statistical procedure for determining whether a statistically significant change has occurred. The Regional Administrator will specify such a procedure in the facility permit if he finds that the alternative procedure reasonably balances the probability of falsely identifying a noncontaminating regulated unit and the probability of failing to identify a contaminating regulated unit in a manner that is comparable to that of the statistical procedure described in paragraph (h)(1)(i) of this section.

(2) In all other situations in a detection monitoring program and in a compliance monitoring program, the owner or operator must use a statistical procedure providing reasonable confidence that the migration of hazardous constituents from a regulated unit into and through the aquifer will be indicated. The Regional Administrator will specify a statistical procedure in the facility permit that he finds:

(i) Is appropriate for the distribution of the data used to establish background values or concentration limits; and

(ii) Provides a reasonable balance between the probability of falsely identifying a non-contaminating regulated unit and the probability of failing to identify a contaminating regulated unit.

§264.98 Detection Monitoring Program

An owner or operator required to establish a detection monitoring program under this subpart must, at a minimum, discharge the following responsibilities:

(a) The owner or operator must monitor for indicator parameters (e.g., specific conductance, total organic carbon, or total organic halogen), waste constituents, or reaction products that provide a reliable indication of the presence of hazardous constituents in groundwater. The Regional Administrator will specify the parameters or constituents to be monitored in the facility permit, after considering the following factors:

(1) The types, quantities, and concentrations of constituents in wastes managed at the regulated unit;

(2) The mobility, stability, and persistence of waste constituents or their reaction products in the unsaturated zone beneath the waste management area;

(3) The detectability of indicator parameters, waste constituents, and reaction products in groundwater; and

(4) The concentrations or values and coefficients of variation of proposed monitoring parameters or constituents in the groundwater background.

(b) The owner or operator must install a groundwater monitoring system at the compliance point as specified under §264.95. The groundwater monitoring system must comply with §464.97(a)(2), (b), and (c).

(c) The owner or operator must establish a background value for each monitoring parameter or constituent specified in the permit pursuant to paragraph (a) of this section. The permit will specify the background values for each parameter to be used to calculate the background values.

(1) The owner or operator must comply with §264.97(g) in developing the data base used to determine background values.

(2) The owner or operator must express background values in a form necessary for the determination of statistically significant increases under §264.97(h).

(3) In taking samples used in the determination of background values, the owner or operator must use a groundwater monitoring system that complies with §264.97(a)(1), (b), and (c).

(d) The owner or operator must determine groundwater quality at each monitoring well at the compliance point at least semi-annually during the active life of a regulated unit (including the closure period) and the post-closure care period. The owner or operator must express the groundwater quality at each monitoring well in a form necessary for the determination of statistically significant increases under §264.97(h).

(e) The owner or operator must determine the groundwater flow rate and direction in the uppermost aquifer at least annually.

(f) The owner or operator must use procedures and methods for sampling and analysis that meet the requirements of §264.97(d) and (e).

(g) The owner or operator must determine whether there is a statistically significant increase over background values for any parameter or constituent specified in the permit pursuant to paragraph (a) of this section each time he determines groundwater quality at the compliance point under paragraph (d) of this section.

(1) In determining whether a statistically significant increase has occurred, the owner or operator must compare the groundwater quality at each monitoring well at the compliance point for each parameter or constituent to the background value for that parameter or constituent, according to the statistical procedure specified in the permit under §264.97(h).

(2) The owner or operator must determine whether there has been a statistically significant increase at each monitoring well at the compliance point within a reasonable time period after completion of sampling. The Regional Administrator will specify that time period in the facility permit, after considering the complexity of the statistical test and the availability of laboratory facilities to perform the analysis of groundwater samples.

(h) If the owner or operator determines, pursuant to paragraph (g) of this section, that there is a statistically significant increase for parameters or constituents specified pursuant to paragraph (a) of this section at any monitoring well at the compliance point, he must:

(1) Notify the Regional Administrator of this finding in writing within seven days. The notification must indicate what parameters or constituents have shown statistically significant increases;

(2) Immediately sample the groundwater in all monitoring wells and determine the concentration of all constituents identified in Appendix VIII of Part 261 of this chapter that are present in groundwater;

(3) Establish a background value for each Appendix VIII constituent that has been found at the compliance point under paragraph (h)(2) of this section, as follows:

(i) The owner or operator must comply with §264.97(g) in developing the data base used to determine background values;

(ii) The owner or operator must express background values in a form necessary for the determination of statistically significant increases under §264.97(h); and

(iii) In taking samples used in the determination of background values, the owner or operator must use a groundwater monitoring system that complies with §264.97(a)(1), (b), and (c).

(4) Within 90 days, submit to the Regional Administrator an application for a permit modification to establish a compliance monitoring program meeting the requirements of §264.99. The application must include the following information:

(i) An identification of the concentration of any Appendix VIII constituents found in the groundwater at each monitoring well at the compliance point;

(ii) Any proposed changes to the groundwater monitoring system at the facility necessary to meet the requirements of §264.99;

(iii) Any proposed changes to the monitoring frequency, sampling and analysis procedures or methods, or statistical procedures used at the facility necessary to meet the requirements of §264.99;

(iv) For each hazardous constituent found at the compliance point, a proposed concentration limit under §264.94(a)(1) or (2), or a notice of intent to seek a variance under §264.94(b); and

(5) Within 180 days, submit to the Regional Administrator:

(i) All data necessary to justify any variance sought under §264.94(b); and

(ii) An engineering feasibility plan for a corrective action program necessary to meet the requirements of §264.100, unless:

(A) All hazardous constituents identified under paragraph (h)(2) of this section are listed in Table 1 of §264.94 and their concentrations do not exceed the respective values given in that Table; or

(B) The owner or operator has sought a variance under §264.94(a) for every hazardous constituent identified under paragraph (h)(2) of this section.

(i) If the owner or operator determines, pursuant to paragraph (g) of this section, that there is a statistically significant increase of parameters or constituents specified pursuant to paragraph (a) of this section at any monitoring well at the compliance point, he may demonstrate that a source other than a regulated unit caused the increase or that the increase resulted from error in sampling, analysis, or evaluation. While the owner or operator may make a demonstration under this paragraph in addition to, or in lieu of, submitting a permit modification application under paragraph (h)(4) of this section, he is not relieved of the requirement to submit a permit modification application within the time specified in paragraph (h)(4) of this section unless the demonstration made under this paragraph successfully shows that a source other than a regulated unit caused the increase or that the increase resulted from error in sampling, analysis, or evaluation. In making a demonstration under this paragraph, the owner or operator must:

(1) Notify the Regional Administrator in writing within seven days of determining a statistically significant increase at the compliance point that he intends to make a demonstration under this paragraph;

(2) Within 90 days, submit a report to the Regional Administrator which demonstrates that a source other than a regulated unit caused the increase, or that the increase resulted from error in sampling, analysis, or evaluation;

(3) Within 90 days, submit to the Regional Administrator an application for a permit modification to make any appropriate changes to the detection monitoring program at the facility; and

(4) Continue to monitor in accordance with the detection monitoring program established under this section.

(j) If the owner or operator determines that the detection monitoring program no longer satisfies the requirements of this section, she/he must, within 90 days, submit an application for a permit modification to make any appropriate changes to the program.

(k) The owner or operator must assure that monitoring and corrective action measures necessary to achieve compliance with the groundwater protection standard under §264.92 are taken during the term of the permit.

§264.99 Compliance Monitoring Program

An owner or operator required to establish a compliance monitoring program under this subpart must, at the minimum, discharge the following responsibilities:

(a) The owner or operator must monitor the groundwater to determine whether regulated units are in compliance with the groundwater protection standard under §264.92. The Regional Administrator will specify the groundwater protection standard in the facility permit, including:

(1) A list of the hazardous constituents identified under §264.93;

(2) Concentration limits under §264.94 for each of those hazardous constituents;

(3) The compliance point under §264.95; and

(4) The compliance period under §264.96.

(b) The owner or operator must install a groundwater monitoring system at the compliance point as specified under §264.95. THe groundwater monitoring system must comply with §264.97(a)(2), (b), and (c).

(c) Where a concentration limit established under paragraph (a)(2) of this section is based on background groundwater quality, the Regional Administrator will specify the concentration limit in the permit as follows:

(1) If there is a high temporal correlation between upgradient and compliance point concentrations of the hazardous constituents, the owner or operator may establish the concentration limit through sampling at upgradient wells each time groundwater is sampled at the compliance point. The Regional Administrator will specify the procedures used for determining the concentration limit in this manner in the permit. In all other cases, the concentration limit will be the mean of the pooled data on the concentration of the hazardous constituent.

(2) If a hazardous constituent is identified in Table 1 under §264.94 and the difference between the respective concentration limit in Table 1 and the background value of that constituent under §264.97(g) is not statistically significant, the owner or operator must use the background value of the constituent as the concentration limit, in determining whether this difference is statistically significant, the owner or operator must use a statistical procedure providing reasonable confidence that a real difference will be indicated. The statistical procedure must:

(i) Be appropriate for the distribution of the data used to establish background values; and

(ii) Provide a reasonable balance between the probability of falsely identifying a significant difference and the probability of failing to identify a significant difference.

(3) The owner or operator must:

(i) Comply with §264.97(g) in developing the data base used to determine background value;

(ii) Express background values in a form necessary for the determination of statistically significant increases under §264.97(h); and

(iii) Use a groundwater monitoring system that complies with §264.97(a)(1), (b), and (c).

(d) The owner or operator must determine the concentration of hazardous constituents in groundwater at each monitoring well at the compliance point at least quarterly during the compliance period. The owner or operator must express the concentration at each monitoring well in a form necessary for the determination of statistically significant increases under §264.97(h).

(e) The owner or operator must determine the groundwater flow rate and direction in the uppermost aquifer at least annually.

(f) The owner or operator must analyze samples from all monitoring wells at the compliance point for all constituents contained in Appendix VIII of Part 261 of this chapter at least annually to determine whether additional hazardous constituents are present in the uppermost aquifer. If tne owner or operator finds Appendix VIII constituents in the groundwater that are not identified in the permit as hazardous constituents, the owner or operator must report the concentrations of these additional constituents to the Regional Administrator within seven days after completion of the analysis.

(g) The owner or operator must use procedures and methods for sampling and analysis that meet the requirements of §264.907(d) and (e).

(h) The owner or operator must determine whether there is a statistically significant increase over the concentration limits for any hazardous constituents specified in the permit pursuant to paragraph (a) of this section each time he determines the concentration of hazardous constituents in groundwater at the compliance point.

(1) In determining whether a statistically significant increase has occurred, the owner or operator must compare the groundwater quality at each monitoring well at the compliance point for each hazardous constituent to the concentration limit for that constituent according to the statistical procedures specified in the permit under §264.97(h).

(2) The owner or operator must determine whether there has been a statistically significant increase at each monitoring well at the compliance point, within a reasonable time period after completion of sampling. The Regional Administrator will specify that time period in the facility permit, after considering the complexity of the statistical test and the availability of laboratory facilities to perform the analysis of groundwater samples.

(i) If the owner or operator determines, pursuant to paragraph (h) of this section, that the groundwater protection standard is being exceeded at any monitoring well at the point of compliance, he must:

(1) Notify the Regional Administrator of this finding in writing within seven days. The notification must indicate what concentration limits have been exceeded.

(2) Submit to the Regional Administrator an application for a permit modification to establish a corrective action program meeting the requirements of §264.100 within 180 days, or within 90 days if an engineering feasibility study has been previously submitted to the Regional Administrator under §264.98(h)(5). The application must, at a minimum, include the following information:

(i) A detailed description of corrective actions that will achieve compliance with the groundwater protection standard specified in the permit under paragraph (a) of this section; and

(ii) A plan for groundwater monitoring program that will demonstrate the effectiveness of the corrective action. Such a groundwater monitoring program may be based on a compliance monitoring program developed to meet the requirements of this section.

(j) If the owner or operator determines, pursuant to paragraph (h) of this section, that the groundwater protection standard is being exceeded at any monitoring well at the point of compliance, he may demonstrate that a source other than a regulated unit caused the increase or that the increase resulted from error in sampling, analysis or evaluation. While the owner or operator may make a demonstration under this paragraph in addition to, or in lieu of, submitting a permit modification application under paragraph (i)(2) of this section, he is not relieved of the requirement to submit a permit modification application within the time specified in paragraph (i)(2) of this section unless the demonstration made under this paragraph successfully shows that a source other than a regulated unit caused the increase or that the increase resulted from error in sampling, analysis, or evaluation. In making a demonstration under this paragraph, the owner or operator must:

(1) Notify the Regional Administrator in writing within seven days that he intends to mkae a demonstration under this paragraph;

(2) Within 90 days, submit a report to the Regional Administrator which demonstrates that a source other than a regulated unit caused the standard to be exceeded or that the apparent noncompliance with the standards resulted from error in sampling, analysis, or evaluation.

(3) Within 90 days, submit to the Regional Administrator an application for a permit modification to make any appropriate changes to the compliance monitoring program at the facility; and

(4) Continue to monitor in accord with the compliance monitoring program established under this section.

(k). If the owner or operator determines that the compliance monitoring program no longer satisfies the requirements of this section, he must, within 90 days, submit an application for a permit modification to make any appropriate changes to the program.

(l) The owner or operator must assure that monitoring and corrective action measures necessary to achieve compliance with the groundwater protection standard under §264.92 are taken during the term of the permit.

3.1.3 Sampling

The facility permit should include procedures for both evacuating the well prior to sampling and withdrawal of the actual samples from the well. In addition, special sampling procedures may be required such as when high or low density, immiscible organics are present in a separate phase at the site. Techniques for water level measurements will also be specified in the permit. Specific sampling methods are provided in Section 1 of this manual. Refer to Sections 1.2.1.20 through 1.2.1.22 for a discussion of sampling equipment, and Section 1.4.6 for a discussion of sampling methodology.

3.1.4 Analysis

Analytical methods will be specified in the facility permit. Each analytical method is selected with proper regard to the sensitivity, precision, and accuracy required to meet RCRA goals of protecting public health and the environment. Analytical interferences that may result from the expected chemical characteristics of groundwater samples from each individual site must be carefully analyzed. The selection of analytical methods should be limited to those in which no significant interference is probable. The availability of equipment, adequately trained manpower, and instrumentation may influence any selection. Cost is also a legitimate consideration, as long as other analytical considerations are not unduly compromised.

A listing of these Appendix VII constituents and suitable methods from this manual are provided in Tables 3.1.4-1 and 3.1.4-2. Of the Appendix VIII compounds, many are inorganic compounds for which EPA is interested only in the metal species (e.g., nickel in nickel carbonyl, thallium in thallium acetate, vanadium in vanadium pentoxide), and some are unstable in water or do not have analytical methods, and thus do not have to be monitored for (see Table 3.1.4-3).

Before submitting data using these methods, the operator, however, will have to determine the accuracy of the method, using analytical standards to spike samples of the groundwater. The methods included in this document have been carefully reviewed by the Agency and have been found to provide adequate precision and accuracy to meet RCRA groundwater monitoring needs. Any interference that may affect measurements have been noted. A detailed description of the required equipment, reagents, and procedures is provided. Guidance on sample preservation, handling, and quality control measures applicable to each method is also provided.

TABLE 3.1.4-1 METHODS FOR ANALYSIS OF ORGANIC CONSTITUENTS (SW-846 TEST METHODS FOR EVALUATING SOLID WASTES) (U.S. EPA, 1982)

Compound	Method(s)
Acetonitrile	8030, 8240
Acetophenone	8250
2-Acetylaminofluorene	8250
1-Acetyl-2-thiourea	8250, 8330
Acrolein	8030, 8240
Acrylamide	8015, 8240
Acrylonitrile	8030, 8240
Aldrin	8250
Allyl alcohol	8250
3-(alpha-Acetonylbenzyl)-4-hydroxy-coumarin	8250, 8320
4-Aminobiphenyl	8250
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)8a-methoxy-5-methyl-carbamate azirino(2',3':3,4)-pyrrolo-(1,2-a)indole-4,7-dione (ester) (Mitomycin C)	8320
5-(Aminomethyl)-3-isoxazole	8250
Amitrole	8250
Aniline	8250
Aramite	8250
Auramine	8250
Azaserine	8330
Benz(a)anthracene	8100, 8250, 8310
Benz(b)fluoroanthene	8100, 8250, 8310
Benz(c)acridine	8250
Benzene	8020, 8024
Benzenearsonic acid (Phenylarsonic acid)	7060
Benzene, dichloromethyl-	8250
Benzenethiol	8250
Benzenoquinone	8250
Benzidine	8250
Benzo(a)pyrene	8100, 8250, 8310
Benzotrichloride	8120, 8250
Benzyl chloride	8120, 8250
Bis(2-chloroethoxymethane)	8010, 8240
Bis(2-chloroethyl)ether	8010, 8240
Bis(2-chloroisopropyl)ether	8010, 8240
Benzo(j)fluoranthene	8100, 8250
N,N-Bis(2-chloroethyl)-2-naphthylamine	8250
Bis-(chloromethyl) ether	8010, 8240
Bis(2-ethylhexyl) phthalate	8060, 8250

TABLE 3.1.4-1 (Continued)

Compound	Method(s)
Bromoacetone	8240
Bromomethane	8240
4-Bromophenyl phenyl ether	8250
Bromine	8250
2-Butanone peroxide	8250
Butyl benzyl phthalate	8060, 8250
2-sec-Butyl-4,6-dinitrophenol (DNBP)	8040
Carbon disulfide	8240
Carbon tetrachloride	8010, 8240
Chloral	8010
Chlorambucil	8320
Chlordane	8080, 8250
Carbon tetrachloride	8010, 8240
Chlorinated benzenes	8010, 8020, 8240, 8250
Chlorinated biphenyls	8080, 8250
Chlorinated dibenzodioxins	8080, 8250
Chlorinated ethane(s)	8010, 8240
Chlorinated fluorocarbons	8010, 8240
Chlorinated naphthalene(s)	8250
Chlorinated phenol(s)	8040
Chloromethane	8010, 8240
Chloroalkyl ethers	8240, 8250
p-Chloroaniline	8250
Chlorobenzene	8020, 8240
Chlorobenzilate	8250
Chloroform	8010, 8240
p-Chloro-m-cresol	8040
1- Chloro-2,3-epoxybutane	8240
Chloroethyl vinyl ether	8240
Chloromethane	8010, 8240
Chloromethyl methyl ether	8240
2-Chloronaphthalene	8240, 8250
2-Chlorophenol	8040, 8250
1-(o-Chlorophenyl)thiourea	8330
3-Chloropropionitrile	8250
Chrysene	8100, 8250, 8310
Citrus red N	8330
Coal Tars (analyze for PAH)	8100, 8250
Creosote[1]	8100, 8250

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[1] Analyze for phenanthrene and carbazole; if these are present in a ratio between 1.4:1 and 5:1, creosote should be considered present.

TABLE 3.1.4-1 (Continued)

Compound	Method(s)
Cresol(s)	8100, 8250
Cresylic Acid(s)	8040, 8250
Crotonaldehyde	8330
Cyanogen (Dicyanogen)	9010
Cyanogen bromide	9010
Cyanogen chloride	9010
2-Cyclohexyl-4,6-dinitrophenol	8250
Daunomycin	8320
DDD([2,2-bis(p-chlorophenyl-1, 1-dichloroethanel])	8250
DDE([2,2-bis(p-chlorophenyl-1, 1-dichloroethylene])	8250
DDT([1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane])	8250
Diallate	8250
Dibenz[a,h]acridine	8100, 8250
Dibenz[a,j]acridine	8100, 8250
Dibenz[a,h]anthracene (Dibenzo[a,h] anthracene)	8100, 8250
7-H-Dibenzo[c,g]carbazole	8100, 8250
Dibenzo[a,e]pyrene	8100, 8250
Dibenzo[a,h]pyrene	8100, 8250
Dibenzo[a,i]pyrene	8100, 8250
1,2-Dibromo-3-chloropropane (DECP)	8240
1,2-Dibromoethane	8240
Dibromomethane	8240
Di-n-butyl phthalate	8060, 8250
Dichlorobenzene(s)	8010, 8120, 8250
3,3'-Dichlorobenzidene	8020, 8250
1,4-Dichloro-2-butene	8010, 8240
Dichlorodifluoromethane	8010, 8240
Dichloroethane(s)	8010, 8240
1,2-trans-Dichloroethene	8250
1,1-Dichloroethylene	8250
Dichloromethane	8010, 8240
Dichlorophenols	8040, 8250
2,6-Dichlorophenol	8040, 8250
Dichlorophenoxyacetic acid	8150, 8250
Dichlorophenylarsine	7060
Dichloropropane(s)	8240
1,2-Dichloropropane	8240

TABLE 3.1.4-1 (Continued)

Compound	Method(s)
Dichloropropanol	8120, 8250
Dichloropropene(s)	8240
1,3-Dichloropropene	8240
Dieldrin	8250
1,2:3,4-Diepoxybutane	8240
Diethylarsine	7060
O,O-Diethyl-S-methylester phosphorodithioic acid	8250
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	8250
Diethyl phthalate	8250
O,O-Diethyl-O-(2-pyrazinyl) phosphorothioate	8250
Dihydrosafrole	8250
Diethylstilbestrol	8330
3,4-Dihydroxy-alpha-((methylamino) methyl)benzyl alcohol	8330
Diisopropylfluorophosphate (DFP)	8250
Dimethoate	8250
3,3'-Dimethoxybenzidene	8250
p-Dimethylaminoazobenzene	8250
7,12-Dimethylbenz(a)anthracene	8100, 8250
3,3'-Dimethylbenzidine	8250
1,1-Dimethylhydrazine	8250
1,2-Dimethylhydrazine	8250
alpha,alpha-Dimethylphenethylamine	8250
2,4-Dimethylphenol	8040, 8250
Dimethyl phthalate	8250
Dimethyl sulfate	8250
Dinitrobenzene	8090, 8250
4,6-Dinitro-o-cresol	8040, 8250
4,6-Dinitro-o-cresol and salts	8040
2,4-Dinitrophenol	8040
2,4-Dinitrotoluene	8090, 8250
Di-n-octyl phthalate	8090, 8250
1,4-Dioxane	8240
Diphenylamine	8250
1,2-Diphenylhydrazine	8250
Di-n-propylnitrosamine	8250
Disulfoton ethyl carbamate	8220, 8250
Ethyl cyanide	8240
2,4-Dithiobiuret	8250
Endosulfan and metabolites	8250

TABLE 1 (Continued)

Compound	Method(s)
Endrin	8080, 8250
Ethylenebisdithiocarbamate (EBDC)	8250
Ethyleneimine	8250
Ethylene oxide	8240
Ethylenethiourea	8250
Ethyl ether	8015, 8240
Ethyl methacrylate	8250
Ethyl methanesulfonate	8100, 8250
Fluoranthene	8100, 8250
Fluoroacetic acid, sodium salt	8250
Formaldehyde	8240
Formic acid	8250
Halomethane(s)	8240
Heptachlor	8080, 8250
Heptachlor epoxide (alpha, beta, or gamma isomers)	8250
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene	8250
Hexachlorobenzene	8120, 8250
Hexachlorobutadiene	8120, 8250
Hexachloroethane	8010, 8240
Hexachlorocyclopentadiene	8120, 8250
Hexachlorophene	8250
Hexachloropropane	8240
Hexaethyltetraphosphate	8250
Hydrazine	8250
Indeno(1,2,3-cd)pyrene	8100, 8250
Iodomethane	8250
Isobutyl alcohol	8240
Isosafrole	8250
Kepone	8240
Lindane(1,2,3,4,5,6-hexachlorocyclohexane)	8080, 8250
Maleic anhydride	8250
Maleic hydrazide	8250
Malononitrile	8240, 8250
Melphalan	8320
Methacrylonitrile	8240
Methanethiol	8240

TABLE 3.1.4-1 (Continued)

Compound	Method(s)
Methanol	8010, 8240
Methapyralene	8250
Methomyl	8250
Methoxychlor	8060, 8250
2-Methylaziridine	8250
3-Methylcholanthrene	8100, 8250
4,4'-Methylene-bis-(2-chloroaniline)	8250
Methyl ethyl ketone	8015, 8240
Methyl hydrazine	8250
Methyl isobutyl ketone	8015, 8240
2-Methyllactonitrile	8240
Methyl methacrylate	8250
Methyl methanesulfonate	8250
2-Methyl-2-(methylthio)-o-(methylcarbonyl)-propionaldehyde oxime	8250
N-Methyl-N'-nitric-N-nitrosoguanidine	8250
Methyl parathion	8250
Methylthiouracil	8250
Naphthalene	8200, 8250
Naphthoquinone	8090, 8250
1-Naphthylamine	8250
2-Naphthylamine	8250
1-Naphthyl-2-thiourea	8330
Nicotine and salts	8250
p-Nitroaniline	8250
Nitrobenzene	8090, 8250
Nitroglycerine	8250
4-Nitrophenol	8040, 8240
4-Nitroquinoline-1-oxide	8250
Nitrosamine(s)	8250
N-Nitrosodi-n-butylamine	8250
N-Nitrosodiethanolamine	8250
N-Nitrosodiethylamine	8250
N-Nitrosodiemethylamine	8250
N-Nitroso-n-ethylurea	8250
N-Nitrosomethylenthylamine	8250
N-Nitroso-n-methylurea	8250
N-Nitroso-n-methylurethane	8250
N-Nitrosomethylvinylamine	8250
N-Nitrosomorpholine	8250
N-Nitrosonornicotine	8250
N-Nitrosopiperidine	8250
N-Nitrosopyrrolidine	8250
N-Nitrososaposine	8250

TABLE 3.1.4-1 (Continued)

Compound	Method(s)
5-Nitro-o-toluidine	8320
Octadecanoic acid, cadmium salt	7130, 7131
Octamethylpyrophosphoramide (OMPA)	8250
Paraldehyde (trimer of acetaldehyde)	8015, 8240
Parathion	8250
Pentachlorobenzene	8250
Pentachloroethane	8250
Penthachloronitrobenzene (PCNB)	8250
Pentachlorophenol	8040, 8250
1,3-Pentadiene	8240
Phenacetin	8250
Phenol	8040, 8250
Phenylenediamine	8250
Phenylmercury acetate	7440, 7441
N-Phenylthiourea	8330
Phorate	8140
Phosphorodithioic acid esters	8140
Phosphorothioic acid, O,O-dimethyl ester, O-ester with N,N-dimethyl benzene sulfonamide	8060
Phthalic anhydride	8090, 8250
Phthalic acid esters	8060, 8250
2-Picoline	8090, 8250
Pronamide	8250
1,3-Propane sultone	8250
n-Propylamine	8250
Propylthiouracil	8250
2-Propyn-1-ol	8250
Pyridine	8090, 8250
Reserpine	8320
Resorcinol	8250
Saccharin	8250
Safrole	8250
Streptozotocin	8320
Tetrachlorobenzene(s)	8120, 8250
Tetrachloroethane(s)	8010, 8240
Tetrachloroethene	8010, 8240
Tetrachlorophenol	8040, 8250
Tetraethyldithiopyrophosphate	8250
Tetraethyl lead	7420, 7421
Tetraethylpyrophosphate	8250

TABLE 3.1.4-1 (Continued)

Compound	Method(s)
Tetranitromethane	8240
Thioacetamide	8330
Thiosemicarbazide	8330
Thiourea	8330
Thiuram	8320
o-Toluidine hydrochloride (as o-Toluidine)	8250
Toluene	8020, 8024
Toluenediamine	8250
Toluene diisocyanate(s)	8250
Toxaphene	8080, 8250
Tribromomethane	8240
1,2,4-Trichlorobenzene	8250
Trichloroethane	8010, 8240
Trichloroethene(s)	8010, 8240
Trichlorofluoromethene	8010, 8240
Trichloromethanethiol	8250
Trichlorophenol(s)	8040, 8250
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	8150
2,4,5-Trichlorophenoxy propionic acid	8150, 8250
Trichloropropane	8010, 8240
1,2,3,-Trichloropropane	8240
O,O,O-Triethyl phosphorothioate	8250
sym-Trinitrobenzene	8250
Tris(1-azridinyl) phosphine sulfide	8250
Tris(2,3-dibromopropyl) phosphate	8250
Trypan blue	8330
Uracil mustard	8250
Vinyl chloride	8010, 8240
Vinylidene chloride	8010, 8240
Xylene	8020, 8240

TABLE 3.1.4-2 METHODS OF ANALYSIS FOR INORGANIC CONSTITUENTS (SW-846 TEST METHODS FOR EVALUATING SOLID WASTES) (U.S. EPA, 1982).

Compound	Method(s)
Antimony and compounds	6010, 7040, 7041
Arsenic and compounds	6010, 7060, 7061
Barium and compounds	6010, 7080, 7081
Beryllium and compounds	6010, 7090, 7091
Cadmium and compounds	6010, 7090, 7091
Chromium and compounds	6010, 7190, 7191
Chromium: Hexavalent and compounds	7195, 7196, 7197, 7198
Copper and compounds	6010, 7210, 7211
Lead and compounds	6010, 7420, 7421
Mercury and compounds	7470, 7471
Nickel and compounds	6010, 7520, 7521
Osmium and compounds	7550, 7551
Selenium and compounds	6010, 7740, 7741
Silver and compounds	6010, 7760, 7761
Thallium and compounds	6010, 7840, 7841
Vanadium and compounds	6010, 7910, 7911
Zinc and compounds	6010, 7950, 7951
Cyanides and compounds	9010
Sulfides and compounds	9030

TABLE 3.1.4-3 APPENDIX VIII CONSTITUENTS UNSTABLE IN WATER OR WITHOUT ANALYTICAL METHODS.

Carbon Oxyfluoride
Aluminum Phosphide
Phosgene
Methyl isocyanate
Nitrogen dioxide
Zinc Phosphide
Acetyl chloride
Dimethyl carbamoyl chloride
Methyl chloro carbonate
Toluene diisocyanate
Fluorine
Hydrogen Fluoride
Cycasin
Ethylenebisdithiocarbamic acid
2-Fluoroacetamide
Iron Dextran
Lasiocarpine
Mustard Gas
Nitrogen Mustard, N-Oxide, HCl salts
Nitrogen Mustard, and HCl salts
Nitric Oxide
Phosphine

3.2 Land Treatment Monitoring

3.2.1 Background

A monitoring program is an essential component at any land treatment unit, and should be planned to provide assurance of appropriate facility design, act as a feedback loop to furnish guidance on improving unit management, and indicate the rate at which the treatment capacity is being approached. Since many assumptions must be made in the design of a land treatment unit, monitoring can be used to verify whether the initial data and assumptions were correct or if design or operational changes are needed. Monitoring cannot be substituted for careful design based on the fullest reasonable understanding of the effects of applying hazardous waste to the soil; however, for existing Hazardous Waste Land Treatment (HWLT) units (which must retrofit to comply with regulations), monitoring can provide much of the data base needed for demonstrating treatment.

Figure 3.2.1 shows the topics to be considered when developing a monitoring program. The program must be developed to provide the following assurances:

(1) that the waste being applied does not deviate significantly from the waste for which the unit was designed;

(2) that waste constituents are not leaching from the land treatment area in unacceptable concentrations;

(3) that groundwater is not being adversely affected by the migration of hazardous constituents of the waste(s); and

(4) that waste constituents will not create a food chain hazard if crops are harvested.

3.2.1.1 Treatment Zone Concept

As is depicted in Fig. 3.2.1.1, the entire land treatment operation and monitoring program revolves about a central component, the treatment zone. Concentrating on the treatment zone is a useful approach to describing and monitoring a land treatment system. The treatment zone is the soil to which wastes are applied or incorporated; HWLT units are designed so that degradation, transformation and immobilization of hazardous constituents and their metabolites occurs within this zone. In practice, setting a boundary to the treatment zone is difficult. In choosing the boundaries of the treatment zone soil forming processes and the associated decrease in biological activity with depth should be considered. According to soil taxonomists, the lower limit of a soil must be set at the lower limit of biologic activity or rooting of native perennial plants, typically about 1 to 2 m (USDA, 1975). Since biological degradation of waste organics is often the primary objective in land treatment, the lower boundary of the treatment zone should not exceed the lower boundary of the soil. Current land treatment regulations place the lower limit of the treatment zone at 1.5 m (EPA, 1982a).

The choice of a lower boundary must be modified where shallow groundwater or perched water can encroach on this zone and thus increase the likelihood of contaminant leaching. A distance of 1 m is the required minimum separation between the bottom of the treatment zone and the seasonal high water table (EPA, 1982a). From soil physics considerations, this separation is necessary because the capillary fringe above the water table, resulting in elevated soil moisture content, is often observed to rise as much as 50 to 75 cm. A second reason for a 1-m separation is that the height of the seasonal high water table is generally an estimate based on limited observation and there may be periods when the saturated zone is at a higher elevation.

A final aspect of the treatment zone that should be considered is the rise in land surface elevation which may result from the accumulation of nondegradable waste solids. In some cases, this rise can be significant and the choice must be made whether to continually redefine the lower treatment zone boundary or define the lower boundary as a static value based on the original land surface elevation. The latter is the logical choice. If the lower boundary were continuously redefined, the waste material remaining below the redefined boundary would then be considered unacceptable since waste constituents must be degraded, transformed or immobilized within the treatment zone.

After considering the various aspects of the treatment zone, the generalized definition is the zone of waste and soil in which degradation, transformation and/or immobilization occurs, extending no more than 1.5 m below the original land surface and separated by at least 1 m from the seasonal high water table (EPA, 1982a). What constitutes "complete" treatment varies according to the specific hazardous constituent and the degree to which the constituent and its metabolites must be degraded or immobilized to prevent both short and long-term harm to human health or the environment. Where data are available, the required level of treatment may be relatively easy to designate; however, if data are lacking or inconclusive, the desired level of treatment must be resolved through laboratory, greenhouse, and/or field testing.

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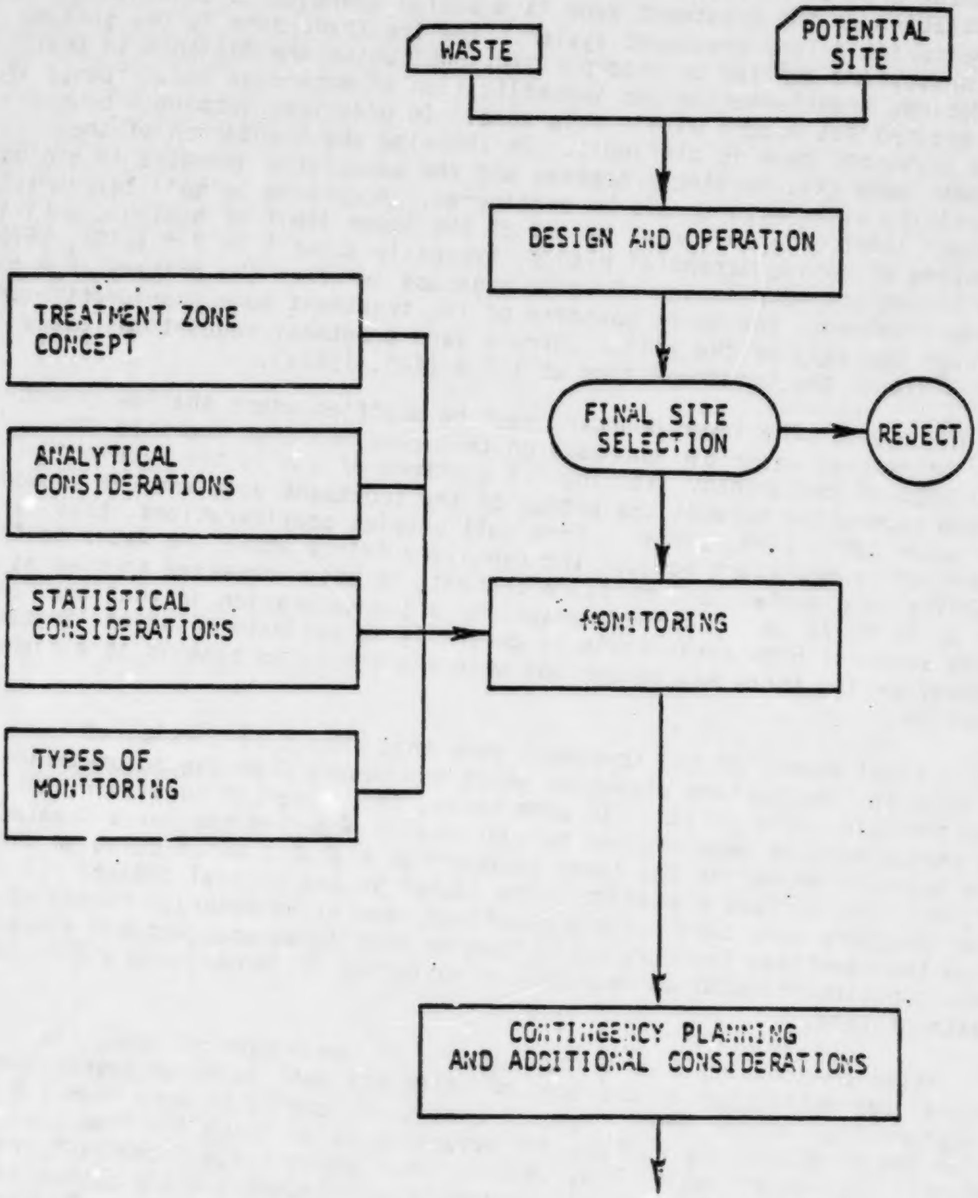
WASTE
POTENTIAL SITE
DESIGN AND OPERATION
TREATMENT ZONE CONCEPT
ANALYTICAL CONSIDERATIONS
STATISTICAL CONSIDERATIONS
TYPES OF MONITORING
FINAL SITE SELECTION
REJECT
MONITORING
CONTINGENCY PLANNING AND ADDITIONAL CONSIDERATIONS

Figure 3.2.1 Topics to be Considered in Developing a Monitoring Program for an HWLT Unit.

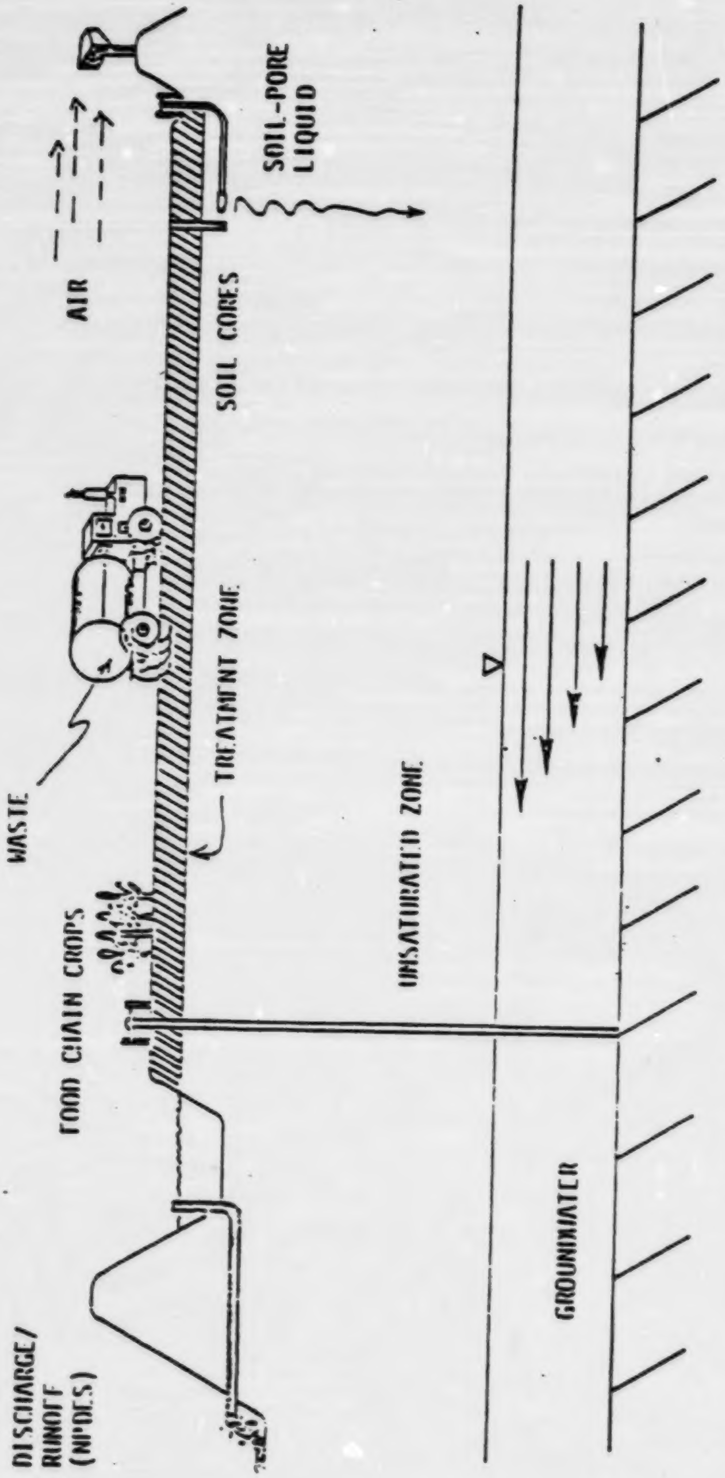
DISCHARGE/
RUNOFF
(NPDES)
FOOD CHAIN CROPS
WASTE
TREATMENT ZONE
AIR
SOIL CORES
SOIL-PORE
LIQUID
UNSATURATED ZONE
GROUNDWATER

Figure 3.2.1.1. Various Types of Monitoring for Land Treatment Units.

3.2.2 Regulatory Definition

The current regulations (EPA, 1982a) require the following types of monitoring:

(1) Groundwater detection monitoring to determine if a leachate plume has reached the edge of the waste management area (40 CFR 264.98).

(2) Groundwater compliance monitoring to determine if the facility is complying with groundwater protection standards for hazardous constituents (40 CFR 264.99).

(3) Soil pH and concentration of cadmium in the waste when certain food-chain crops are grown on HWLTs where cadmium is disposed (40 CFR 264.276).

(4) Unsaturated zone including soil cores and soil-pore liquid monitoring to determine if hazardous constituents are migrating out of the treatment zone (40 CFR 246.278).

(5) Waste analysis of all types of waste to be disposed at the HWLT (40 CFR 264.13).

3.2.3 Monitoring and Sampling Strategy

As discussed earlier the monitoring program centers around the treatment zone.

The frequency of sampling and the parameters to be analyzed depend on the characteristics of the waste being disposed, the physical layout of the unit, and the surface and subsurface characteristics of the site. Table 3.2.3 provides guidance for developing an operational monitoring program. Each of the types of monitoring are discussed below.

3.2.3.1 Waste Monitoring

Waste streams need to be routinely sampled and tested to check for changes in composition. A detailed description of appropriate waste sampling techniques, tools, procedures, etc. is provided in Section 1 of this manual. These procedures should be followed during all waste sampling events. Waste Analysis Methods are provided in this manual. The analyst should choose the appropriate method based on each waste and specific constituents to be tested for.

TABLE 3.2.3. GUIDANCE FOR AN OPERATIONAL MONITORING PROGRAM AT HWLT UNITS

Media to be Monitored	Purpose	Sampling Frequency	Number of Samples	Parameters to be Analyzed
Waste	Quality Change.	Quarterly composites if continuous stream; each batch if intermittent generation.	One	At least rate and capacity limiting constituents, plus those within 25% of being limiting, principal hazardous constituents, pH and EC.
Soil cores (unsaturated zone)	Determine slow movement of hazardous constituents.	Quarterly	One composited from two per 1.5 ha (4 ac); minimum of 3 composited from 6 per uniform area.	All hazardous constituents in the waste or the principal hazardous constituents, metabolites of hazardous constituents, and nonhazardous constituents of concern.
Soil-pore liquid (unsaturated zone)	Determine highly mobile constituents.	Quarterly, preferably following leachate generating precipitation snowmelt.	One composited from two samplers per 1.5 ha (4 ac); minimum of 3 composited from 6 per uniform area.	All hazardous constituents in the waste or the principal hazardous constituents, mobile metabolites of hazardous constituents, and important mobile nonhazardous constituents.
Groundwater	Determine mobile constituents.	Semiannually	Minimum of four suggested--one upgradient, three downgradient.	Hazardous constituents and metabolites or select indicators.
Vegetation (if grown for food chain use).	Phytotoxic and hazardous transmitted constituents (food chain hazards).	Annually or at harvests.	One per 1.5 ha (4 ac) or three of processed crop before sales.	Hazardous metals and organics and their metabolites.
Runoff water	Soluble or suspended constituents.	As required for NPDES permit.	As permit requires, or one.	Discharge permit and background parameters plus hazardous organics.
Soil in the treatment zone	Determine degradation, pH, nutrients, and rate and capacity limiting constituents.	Quarterly	7-10 composited to one per 1.5 ha (4 ac).	
Air	Personnel and population health hazards.	Quarterly	Five	Particulates (adsorbed hazardous constituents) and hazardous volatiles.

3.2.3.1.1 Waste Sampling Strategy

The frequency at which a waste needs to be sampled and the parameters to be analyzed depends greatly on the variables that influence the quantity and quality of the waste. When waste is generated in a batch, as would be expected from an annual or biannual cleanout of a lagoon or tank, the waste should be fully characterized prior to each application. When the waste is generated more nearly continuously, samples should be collected and composited based on a statistical design over a period of time to assure that the waste is of a uniform quality. For example, wastes which are generated continuously could be sampled weekly or daily on a flow proportional basis and composited and analyzed quarterly or monthly. When no changes have been made in the operation of the plant or the treatment of the waste which could significantly alter concentration of waste constituents, the waste should, at a minimum, be analyzed for (1) the constituents that restrict the annual application rates (RLC) and the allowable cumulative applications (CLC), (2) the constituents that are within 25% of the level at which they would be limiting, and (3) all other hazardous constituents that have been shown to be present in the waste in the initial waste characterization. Since synergism and antagonism as well as unlisted waste metabolites can create hazards that cannot be described by chemical analysis alone, routine multigenicity testing may be performed if the treatment demonstration has indicated a possible problem. In addition, waste should be analyzed as soon as possible after a change in operations that could affect the waste characteristics.

3.2.3.2 Groundwater Monitoring and Sampling Strategy

To assure that irreparable groundwater damage does not occur as a result of HWLT, it is necessary that the groundwater quality be monitored. Groundwater monitoring supplements the unsaturated zone monitoring system, but does not replace it. A contamination problem first detected in the leachate water may indicate the need to alter the management program and groundwater can then be observed for the same problem. It is through the successful combination of these two systems that accurate monitoring of vertically moving constituents can be achieved. Groundwater monitoring requirements are discussed in Section 3.1 of this manual.

3.2.3.3 Vegetation Monitoring and Sampling Strategy

Where food chain crops are to be grown, analysis of the vegetation at the HWLT unit will aid in assuring that harmful quantities of metals or other waste constituents are not being accumulated by, or adhering to surfaces of, the plants. Although a safety demonstration before planting is required (EPA, 1982a), operational monitoring is recommended to verify that crop contamination has not occurred. Vegetation monitoring is an important measurement during the post closure period where the area may possibly be used for food or forage production. Sampling should be done annually, or at each harvest. The concentrations of metals and other constituents in the vegetation will change with moisture content, stage of growth, and the part of the plant sampled, and thus results must be carefully interpreted. The number of samples to analyze is again based on a sliding scale similar to that used for sampling soils. Forage samples should include all aerial plant parts, and the edible parts of grain, fruit, or vegetation crops should be sampled separately.

3.2.3.4 Runoff Water Monitoring and Sampling Strategy

If runoff water analyses are needed to satisfy NPDES permit conditions (EPA, 1981), a monitoring program should be instituted. This program would not be covered under RCRA hazardous waste land disposal requirements, but it would be an integral part of facility design. The sampling and monitoring approach will vary depending on whether the water is released as a continuous discharge or as a batch discharge following treatment to reduce the hazardous nature of the water. Constituents to be analyzed should be specified in the NPDES permit.

Where a relatively continous flow is anticipated, sampling must be flow proportional. A means of flow measurement and an automated sampling device are a reasonable combination for this type of monitoring. Flow can be measured using a weir or flume (USDA, 1979) for overload flow water pretreatment systems and packaged water treatment plants while in-line flow measurement may be an additional option on the packaged treatment systems. The sampling device should be set up to obtain periodic grab samples as the water passes through the flow rate measuring device. A number of programmable, automated samplers which can take discreet or composite samples are on the market and readily available.

For batch treatment, such as mere gravity separation or mechanically aerated systems, flow is not so important as is the hazardous constituent content of each batch. Sampling before discharge would, in this case, involve manual pond sampling, using multiple grab samples. The samples would preferably represent the entire water column to be discharged in each batch rather than a single depth increment. Statistical procedures should again be used for either treatment and discharge approach.

3.2.3.5 Unsaturated Zone Monitoring and Sampling Strategy

Unsaturated zone monitoring, soil core sampling technique and soil-pore liquid sampling technique are discussed in detail in Section 1.4.7, Land Treatment Sampling.

3.2.3.6 Treatment Zone Monitoring and Sampling Strategy

Treatment zone monitoring of land treatment units is needed for two purposes. One main purpose is to monitor the degradation rate of the organic fraction of the waste material and parameters significantly affecting waste treatment. Samples are needed at periodic intervals after application to be analyzed for residual waste or waste constituents. Such measurements need to be taken routinely as specified by a soil scientist. These intervals may vary from weekly to semi-annually depending on the nature of the waste, climatic conditions, and application scheduling. The second major function of treatment zone samples is to measure the rate of accumulation of conserved waste constituents as it relates to facility life.

3.2.3.6.1 Sampling Procedures

See Section 1.4.7.

3.2.3.6.2 Scheduling and Number of Soil Samples

The sampling schedule and number of samples to be collected may depend on management factors, but a schedule may be conveniently chosen to coincide with unsaturated zone soil core sampling. For systems which will be loaded heavily in a short period, more (and more frequent) samples may be needed to assure that the waste is being applied uniformly, and that the system is not being overloaded. About seven to ten samples from each selected 1.5 ha (4 ac) area should be taken to represent the treatment zone, and these should be composited to obtain a single sample for analysis. In addition, if there are evidently anomalous "hot spots," these should be sampled and analyzed separately.

3.2.3.7 Air Monitoring and Sampling Strategy

The need for air monitoring at a land treatment unit is not necessarily dictated only by the chemical characteristics of the waste. Wind dispersal of particulates can mobilize even the most immobile, nonvolatile hazardous constituents. Therefore, it is suggested that land treatment air emissions be monitored at frequent intervals to ensure the health and safety of workers and adjacent residents. This effort may be relaxed if the air emissions are positively identified as innocuous compounds or too low in concentration to have any effect. Although air monitoring is not currently required, it is strongly suggested since this is a likely pathway for pollutant losses from a land treatment unit.

Sampling generally involves drawing air over a known surface area, at a known flow rate for a specified time interval. Low molecular weight volatiles may be trapped by solid sorbents, such as Tenax-GC. The high molecular weight compounds may be sampled by Florisil, glass fiber filters, or polyurethane foam.

3.2.4 Analysis

3.2.4.1 Analytical Considerations

Parameters to be measured include pH, soil fertility, residual concentrations of degradable rate limiting constituents (RLC), and the concentrations of residuals which limit the life of the disposal site (CLC), plus those which if increased in concentration by 25% would become limiting. Hazardous constituents of concern should also be monitored. Based on the data obtained, the facility management or design can be adjusted or actions taken as needed to maintain treatment efficiency. Projections regarding facility life can also be made and compared to original design projections. Since the treatment zone acts as an integrator of all effects, the data can be invaluable to the unit operator.

The analyst should use specific methods in this manual for determining hazardous waste constituents.

3.2.4.2 Response to Detection of Pollutant Migration

If significant concentrations of hazardous constituents (or PHCs) are observed below the treatment zone, the following modifications to unit operations should be considered to maximize treatment within the treatment zone:

(1) alter the waste characteristics;

(2) reduce waste application rate;

(3) alter the method or timing of waste applications;

(4) cease application of one or more particular wastes at the unit;

(5) revise cultivation or management practices; and

(6) alter the characteristics of the treatment zone, particularly soil pH or organic matter content.

Hazardous constituents movement below the treatment zone may result from improper unit design, operation, or siting. Problems related to unit design and operation can often be easily corrected, while serious problems resulting from a poor choice of site are more difficult to rectify. Certain locational "imperfections" may be compensated for through careful unit design, construction, and operation.

3.2.5 References

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3.3 Incineration

3.3.1 Introduction

As part of the Resource Conservation and Recovery Act, the U.S. Environmental Protection Agency has promulgated interim, final, and proposed regulations for the owners/operators of facilities that treat hazardous wastes by incineration, to ensure that these incinerators are operated in an environmentally responsible manner. The regulations cover a range of activities including operating performance standards, waste analysis, trial burns, monitoring and inspections, recordkeeping and reporting, emission control criteria, fugitive emissions control, and closure of the facility. The specific details governing each facility are authorized via permit.

In the permitting process, responsible officials are obligated to use their best professional judgment to determine the performance parameters that must be set for each facility. The primary criterion upon which all operational specifications are based is the destruction and removal efficiency (DRE) of the incinerators. This value, defined in terms of waste input levels and stack output levels of the principal organic hazardous constituents (POHCs) designated in the trial burn permitting process, must be 99.99% or more, in order to meet permitting standards for hazardous waste incineration.

Technical advisory information is contained in the documents "Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incineration Units" (see reference 1) and "Engineering Handbook for Hazardous Waste Incineration" (see reference 2). Those documents provide engineering information on waste and effluent characterization, incinerator design, control technology, facilities requirements, environmental impacts, and cost evaluations. Additional documentation for permit writers and for facility owners/operators is available that will address specific points raised during the permitting process.

This section (3.3) of the manual addresses the specific sampling and analysis strategies and methods to be used when measuring the levels of POHCs in the various streams of an incinerator facility: inlet waste, stack gas, process water, fly ash, bottom ash, etc. This compilation of sampling and analysis methods expands upon and augments the information contained in the "Guidance Manual for Evaluating Permit Applications for Hazardous Waste Incineration Units." This section is an initial attempt to gather together selected sampling and analysis procedures for the benefit of owners/operators of hazardous waste incineration units, permit application writers, permit reviewers, and chemical analysts. The information it contains should therefore be considered to be a guideline rather than a prescription. These protocols lack definitive data on accuracy and precision due to their hitherto limited use. As new data are developed they will be made available, through updated versions of this manual or other sources. It is important that users of these protocols provide information on verified techniques, new procedures, and other relevant matters to the EPA so that updates can be provided.

The regulatory requirements for sampling and analysis strategies are briefly reviewed (Section 3.3.2), with emphasis on the data needs for trial burns. During trial burns, sampling and analysis methods should allow measurement of those POHCs expected to be present in the effluents. Also during trial burns, the waste samples are characterized to establish limits for those waste compositions that may be incinerated. During routine facility operation, the incoming wastes are examined periodically to ascertain whether the composition of the waste has changed. Some gaseous species, such as carbon monoxide, are monitored continuously as an indicator of the combustion efficiency of the process. Periodically, at a frequency not specified in the current regulations, the influent and effluent streams may be tested to monitor compliance with the DRE criterion and general incinerator performance.

Section 3.3.3 discusses the strategies used to prepare sampling and analysis plans to meet the regulatory requirements. These strategies include approaches to the selection of those POHCs likely to be present in the waste streams and combustion effluents. Strategies for monitoring of indicator species and characterization of liquid and solid effluents are also included.

Specific sampling, preparation, and analysis methodologies are addressed in terms of the various types of streams and sample media which will be encountered. As an auxiliary to these sections, Section 3.3.4 describes sampling methods that will aid in the collection of high quality sampling and analysis data. This section also discusses the reporting and documentation concerns for the sampling and analysis of incinerators. Other aspects of these requirements are fully discussed in the permit writers guidance document (reference 1).

3.3.2 Regulatory Definition

The following material is reproduced verbatim from the Federal Register.

§264.341 Waste Analysis

(a) As a portion of a trial burn plan required by §122.27(b) of this Chapter or with Part B of his permit application, the owner or operator must have included an analysis of his waste feed sufficient to provide all information required by §122.27(b)(2) or §122.25(b)(5) of this Chapter.

(b) Throughout normal operation the owner or operator must conduct sufficient waste analysis to verify that waste feed to the incinerator is within the physical and chemical composition limits specified in his permit - under §264.345(b).

§265.341 Waste Analysis

In addition to the waste analyses required by §265.13, the owner or operator must sufficiently analyze any waste which he has not previously burned in his incinerator to enable him to establish steady state (normal) operating conditions (including waste and auxiliary fuel feed and air flow) and to determine the type of pollutants which might be emitted. At a minimum, the analysis must determine:

(a) Heating value of the waste;

(b) Halogen content and sulfur content in the waste; and

(c) Concentrations in the waste of lead and mercury, unless the owner or operator has written, documented data that show that the element is not present.

(Comment: As required by §265.73, the owner or operator must place the results from each waste analysis, or the documented information, in the operating record of the facility.)

3.3.3 Sampling and Analysis Strategies for Incineration

3.3.3.1 Introduction

Section 3004 of RCRA requires the Administrator of the U.S. EPA to promulgate such performance standards for owners and operators of hazardous waste treatment, storage, and disposal facilities (TSDFs) as may be necessary to protect human health and the environment. Section 3004 standards not only establish the levels of environmental protection that hazardous waste TSDFs must achieve, but are also the criteria against which applications for permits must be measured. The facility standards are thus key elements in the system mandated by RCRA for management of hazardous wastes.

The RCRA regulations that relate specifically to hazardous waste incineration are incorporated in the Code of Federal Regulations, Title 40 (40 CFR), Parts 122, 264, and 265. Under Part 122, EPA Administered Permit Programs, Subpart A presents definitions and general program requirements, while Subpart B specifies the additional requirements for hazardous waste permitting programs under RCRA. Under both Parts 264 (Performance Standards) and 265 (Interim Status Standards), Subpart B presents general facility standards, including general waste characterization requirements, and Subpart O relates specifically to incinerators.

Hazardous Waste Permit Program

The Part 122, Subpart B requirements for hazardous waste incineration permit programs under RCRA require that the owner/operator of an incineration facility must either:

1. Submit results of a trial burn demonstrating facility operating conditions under which the waste can be incinerated in accordance with the Part 264 performance standards, or

2. Submit data based on waste analysis and on other trial or operational burns sufficient to specify operating conditions under which the waste can be incinerated in accordance with the Part 264 performance standards.

NOTE: An exemption to these requirements may be sought in the case of incineration of waste that is hazardous only because it has the characteristic of Ignitability, Corrosivity, or Reactivity (in some cases) under Part 261, Subpart C of the RCRA regulations and that contains insignificant concentrations of hazardous components as defined by Appendix VIII of Part 261.

Sampling and analysis requirements for waste characterization are the same in the case of a trial burn (§122.17) or alternative data submission (§122.25). The analysis of the waste must include:

1. Heating value of the waste (in the form and composition in which it will be burned)

2. Viscosity or physical form

3. Identification and approximate quantification of any hazardous organic constituents that are listed in Appendix VIII of Part 261 and are also known or suspected to be present in the waste

4. Quantification of those hazardous constituents that may be designated as POHCs for purposes of demonstrating compliance with DRE performance standards.

Sampling and analysis requirements for incinerator effluent characterization in the event that a trial burn is conducted include:

1. Quantitative analysis of the stack exhaust gas for concentration (mass emissions) of designated POHCs

2. Continuous monitoring of carbon monoxide in the stack exhaust gas

3. Determination of the excess air level (oxygen/carbon dioxide measurement)

4. Quantitative analysis (in some cases) of the stack exhaust gas for hydrochloric acid for purposes of calculating a removal efficiency and/or emission rate.

It is important to emphasize that most of the sampling and analysis procedures described in this manual relate to trial burns. It is further important to note that only a small fraction of the procedures specifically selected to address individual POHCs will generally be applied in any single trial burn.

For operating burns, the only explicit sampling and analysis requirement is the determination of carbon monoxide in the stack gas. Although the permit writer or the state/local authorities may impose additional monitoring requirements in some instances, it is not anticipated that comprehensive sampling of the stack gas effluent or specific analysis of POHCs will be required, except in trial burn situations.

General Facility Standards

The General Facility Standards present a General Waste Analysis requirement that is identical in the interim status (§265.13) and performance (§264.13) standards. The requirement specifies that the owner or operator must obtain a detailed chemical and physical analysis of a representative sample of waste. At a minimum, the analysis must generate all of the information that must be known to treat, store, or dispose of the waste in accordance with RCRA requirements and/or conditions of an operating permit. In addition to this detailed analysis of a representative waste sample, the owner/operator must "inspect" each shipment of waste to determine whether it matches the identity specified on the manifest. The sampling and analysis or inspection methods to be used must be specified in a written plan, which may become part of a RCRA Subpart B permit application.

Incinerator Standards

The Part 265 Subpart O Incinerator standards (interim) require, in addition to the general waste analysis, that the owner/operator sufficiently analyze any waste that he has not previously burned in his incinerator to enable him to establish normal operating conditions to determine the type of pollutants that might be emitted. The interim status standards for incinerators incorporate no explicit requirements for sampling and analysis of stack gases or other incinerator effluents.

The Part 264 Subpart O Incinerator standards (permitted) include requirements for waste analysis, three performance standards that include implicit sampling and analysis requirements, and also some operating/monitoring/inspection requirements. The waste analysis requirements of the Part 264 regulations are cross-referenced to the Part 122 Hazardous Waste Permit Program regulations and include analysis to determine heating value of the waste, viscosity or physical form, and detailed chemical analysis to identify the POHCs of the waste.

The Part 264 performance standards relate to:

1. Destruction and Removal Efficiency for each POHC designated in the permit. The DRE, defined in terms of the mass emission rate of a POHC in the stack gas vs. the mass feed rate of the sample POHC in the waste, must be 99.99% or more. The DRE performance standard implicitly requires sampling and analysis to quantify the POHCs in the waste and in the stack gas during a trial burn.
2. Limitation on hydrochloric acid emissions from the stack of incinerators. This performance standard implicitly requires sampling and analysis, in some cases, to quantify hydrochloric acid in the stack gas and/or to determine the efficiency of air pollution control devices.
3. Limitation on stack emissions of particulate material to 180 mg/m^3 or less (0.08 gr/SCF or less), corrected to a standard excess air level. This performance standard implies measurement of particulate emission rates.

The sampling and analysis requirements of the Part 264 regulation performance standards are described here as implicit because, during routine operation burns, compliance with specified operating requirements is acceptable in lieu of actual demonstrated compliance with the performance standards. The operating requirements (§264.345) and monitoring/inspection requirements (§264.347), in turn specify that the carbon monoxide level in the stack exhaust gas must be monitored continuously; this is the only explicit chemical sampling and analysis requirement imposed on all operating incinerators by Part 264 regulations. On a case-by-case basis, the permit to operate an incinerator may specify additional operating requirements that necessitate other types of sampling and analysis on a routine basis. The permit may also include requirements for sampling and analysis to demonstrate actual compliance with the performance standards on an annual or other periodic schedule.

3.3.3.2 Waste Characterization Strategy

Sampling

Acquisition of a representative sample of hazardous waste for subsequent chemical analysis is accomplished by preparing a composite of several subsamples of the waste. Sampling equipment and tactics for collection of the subsamples are specified in Section One of this manual and generally involve grab sampling of liter/kilogram-sized portions of waste materials. To ensure that the bulk of the waste is accurately represented by the composite sample, the sampling strategy requires collection of a minimum of four subsamples which provide integration over both the depth and the surface area of the waste as contained in drums, tanks, holding ponds, etc. The composite sample prepared in the field is split into at least three replicate samples prior to shipment to the analytical laboratory. This step is primarily a precaution against breakage or loss of sample, but also provides the potential for a check on the homogeneity of the composite sample.

To ensure that sampling and analysis results will withstand scrutiny, chain-of-custody procedures are incorporated into sampling protocols. The sampling protocols also include explicit provisions for ensuring the safety of the personnel collecting the samples.

Analysis

The overall strategy for waste characterization includes test procedures to determine the characteristics of the waste and analysis procedures to determine the composition of the waste. The analysis procedures for determining the composition of the waste can be divided into three sections:

1. Characteristics
2. Proximate Analysis
3. Specific Analysis

Figure 3.3.3.2 provides an overview of this analytical approach. The discussion below provides a capsule description of each major element of this scheme and the utility of the resulting information in the hazardous waste incineration permitting process.

Characteristics - The characteristics of the waste sample, defined in terms of ignitability, corrosivity, reactivity, and extraction procedure toxicity, will be determined according to the procedures presented in Section Two of this manual. These tests will be performed on a sample from each waste stream unless there is sufficient information from the engineering analysis to indicate that the waste does not meet any of these four criteria.

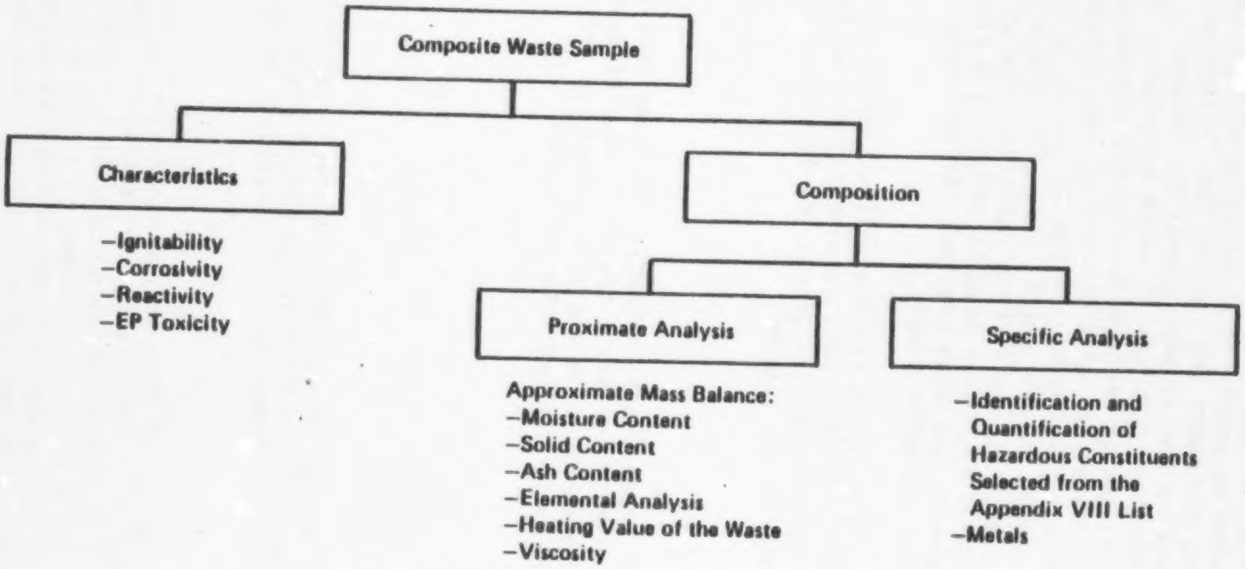
Composite Waste Sample
Characteristics
–Ignitability
–Corrosivity
–Reactivity
–EP Toxicity
Composition
Proximate Analysis
Approximate Mass Balance:
–Moisture Content
–Solid Content
–Ash Content
–Elemental Analysis
–Heating Value of the Waste
–Viscosity
Specific Analysis
–Identification and Quantification of Hazardous Constituents Selected from the Appendix VIII List
–Metals

Figure 3.3.3.2. Overview of the analytical approach for waste characterization.

This information is relevant to the Part 264, Subpart B, General Waste Analysis requirement in that it affects procedures for safely storing, handling, and disposing of the waste at the facility. The data are also relevant to possible exclusion from the trial burn requirements of Part 122. The data on the characteristics of each hazardous waste to which the tests are applicable will generally be available from the waste generator and from manifest or shipping papers received by the facility owner/operator.

Proximate Analysis - The proximate analysis provides data relating to the physical form of the waste and provides an approximate mass balance as to its composition. This analysis includes determination of:

1. Moisture, solid, and ash content
2. Elemental composition (carbon, nitrogen, sulfur, phosphorus, fluorine, chlorine, bromine, iodine to 0.1% level)
3. Heating value of the waste
4. Viscosity.

This information meets the waste analysis requirements of the Part 264, Subpart O regulations, as well as being responsive to the General Waste Analysis requirements of Subpart B. The elemental composition data allow prediction of a high concentration of potentially significant combustion products (NO_x, SO_x, P_2O_5, hydrogen halides, and halogens). These data also facilitate an informed selection of the Appendix VIII hazardous constituents that might be present in the waste by indicating whether the overall waste composition, and hence the types of components present, are consistent with expectations based on best professional judgment. For example, if bromine were not expected to be present in the waste, the organobromine compounds from Appendix VIII would have been excluded from specific analysis based on professional judgment. If bromine were in fact found in the waste at 0.5% by weight, the list of compounds analyzed for should be expanded to include the organobromines. It may also be possible in some cases to rule out some categories of Appendix VIII compounds on the basis of elemental analysis data when conservative professional judgment could not have excluded them.

Specific Analysis - The specific analysis portion of the waste characterization scheme provides qualitative confirmation of the presence and identity of specific compounds and quantitative data, with appropriate quality control measures for the Appendix VIII constituents that might reasonably be expected to be present in the waste based on professional judgment and/or on the results of proximate analysis. It is important to note that specific analysis does not involve screening of every waste sample against the complete Appendix VIII hazardous component list. A preliminary judgment is made as to the compounds or types of compounds that are actually present.

For the specific organic analyses, a high resolution separation technique (fused silica capillary gas chromatography) and a high specificity detection technique (mass spectrometry) are used wherever possible. This approach ensures adequate qualitative and quantitative analysis on a cost-effective basis for a variety of waste types and process chemistries.

Although gas chromatography/mass spectrometry (GC/MS) instrumentation is sophisticated and has a high initial capital cost, it is widely available in contractor laboratories, routine analytical service laboratories, and EPA laboratories. The combination of high specificity and reliable compound identification, high sensitivity, and good quantitative capability, and determination of multiple components in a single analysis, make GC/MS the analytical method of choice for both waste and effluent organic analyses. Alternative organic analysis procedures using gas chromatography with less specific detectors generally require additional sample preparation and multiple analyses and may still prove inadequate in terms of selectivity and elimination of interferences from nontarget compounds. For the inorganic directed analysis, atomic absorption spectroscopy and inductively coupled argon plasma emission spectroscopy (both for metals) and ion chromatography (for anions) are the primary analytical procedures.

The results of the specific analysis will establish that the waste contains the suspected pollutant and will demonstrate the concentration range at which the pollutant may be expected to be found. Specific analysis will also be used to confirm and quantify unexpected hazardous components identified in the survey analysis. These data from the quantitative analysis of confirmed, identified contaminants of documented toxicity (Appendix VIII compounds) are essential for selection of POHCs and prediction of hazardous by-products of combustion.

Selection of POHCs - The criteria for selection of POHCs (typically one to six specific constituents per waste stream) include:

1. The expected difficulty of thermal degradation of the various hazardous organic constituents in the waste
2. The concentration of those constitutents in the waste.

It is anticipated that the designation of POHCs will be negotiated on a case-by-case basis for each permit application. It is important to note that it is not necessarily, nor even generally, true that all Appendix VIII compounds present in the waste will be designated as POHCs for trial burn purposes. The intent is to select a few specific compounds as indicators of satisfactory incinerator performance when burning a particular waste. It is necessary that the compounds selected provide a sufficiently stringent test of the incinerator performance to ensure that incineration of the waste can be carried out in an environmentally sound fashion. This criterion mandates selection of the more thermally stable constituents as POHCs. At the same time, however, it is also necessary that the designated POHCs be present in the waste in sufficiently high concentration that they are capable of being detected in the stack gas at emission levels corresponding to 0.01% or less of their mass feed rate in the waste. This is a particularly important constraint for wastes that are to be incinerated with substantial quantities of auxiliary fuel which effectively dilutes the POHCs in the exhaust gas. Although the burning of auxiliary fuel might not affect the mass emission rate of POHCs, it would lead to an increased volumetric flow of stack gas and thus to a decreased concentration of POHC at the stack. This lower concentration directly affects the detection limit achievable for a given stack gas sample size (e.g., 5 m^3 or 30 m^3).

It is recommended that, whenever possible, the permit writer select POHCs present in the waste at 1000 mg/kg or higher. If it is considered desirable to designate as a POHC a thermally stable compound present at the hundreds of parts per million level, the trial burn permit application must include calculations and supporting data to indicate that 0.01% of the mass feed rate of that component in the waste could in fact be detected in the stack effluent. A waste concentration of 100 mg/kg probably represents a practical lower level below which determination of 99.99% DRE may require extraordinary sampling analysis and quality control procedures, which may significantly increase the sampling and analysis costs for that trial burn.

For a waste material that is a listed hazardous waste under RCRA (40 CFR Part 261 Subpart D), the constituents which caused the Administrator to list the waste as toxic (tabulated in Appendix VII of 40 CFE Part 261) would be logical candidates for designation as POHCs if these constituents were organic chemicals.

3.3.3.3 Stack Gas Effluent Characterization Strategy

The overall strategy for hazardous waste incinerator stack gas effluent characterization to determine compliance with Part 264 performance standards is to collect replicate 3- to 6-hour, 5- to 30-m^3 samples of stack gas using a comprehensive sampling train, such as the EPA Modified Method 5 train (MM5; see Section 1.2.1.8 of this manual), or the EPA/IERL-RTP Source Assessment Sampling System (SASS; see Section 1.2.1.9), or, for the volatile species, the Volatile Organic Sampling Train (VOST; see Section 1.2.1.13). Any of the comprehensive sampling trains provides a sample sufficient for determination of particulate mass loading, concentrations of particulate and low volatility vapor phase organics, and concentrations of particulate and volatile metals. The VOST is used to generate the sample to be analyzed for volatile organic species. Directed analyses for POHCs is performed on these samples. For burns of wastes that could also produce significant emissions of HCl, an MM5 type train is used to collect and quantify HCl in the stack gas.

Figure 2 shows an overview of the analysis scheme for stack gas samples. The same sample (cyclone and particulate catch) can be used for determination of particulate mass loading and subsequent extraction of nonvolatile organic components. Volatile organic components of the stack gas will be collected using the VOST.

The directed analysis shown in Figure 3.3.3.3 is performed on triplicate samples. Although analysis of only two samples would allow an average level of a POHC to be determined, at least three samples should be analyzed so that an error bound for the measured values can be computed. The incremental cost of the replicate sampling and analysis is warranted by the increased confidence in the resulting data; quantitative results from a single sampling and analysis run should not generally be considered as an acceptable indicator of performance.

The survey analysis, which is a qualitative screen of the collected material to ensure that potentially hazardous but unexpected emissions do not go overlooked, need be performed on no more than one stack gas sample. During a trial burn, the oxygen/carbon dioxide levels in the stack gas must be measured using an Orsat analyzer as detailed in 40 CFR Part 60, Appendix A, Method 3 (see reference 3) so that the particulate loading may be corrected to a standard excess air level.

For both trial and operating burns, on-line monitors (nondispersive infrared instruments) are used to provide continuous readings of carbon monoxide levels in the incinerator effluent.

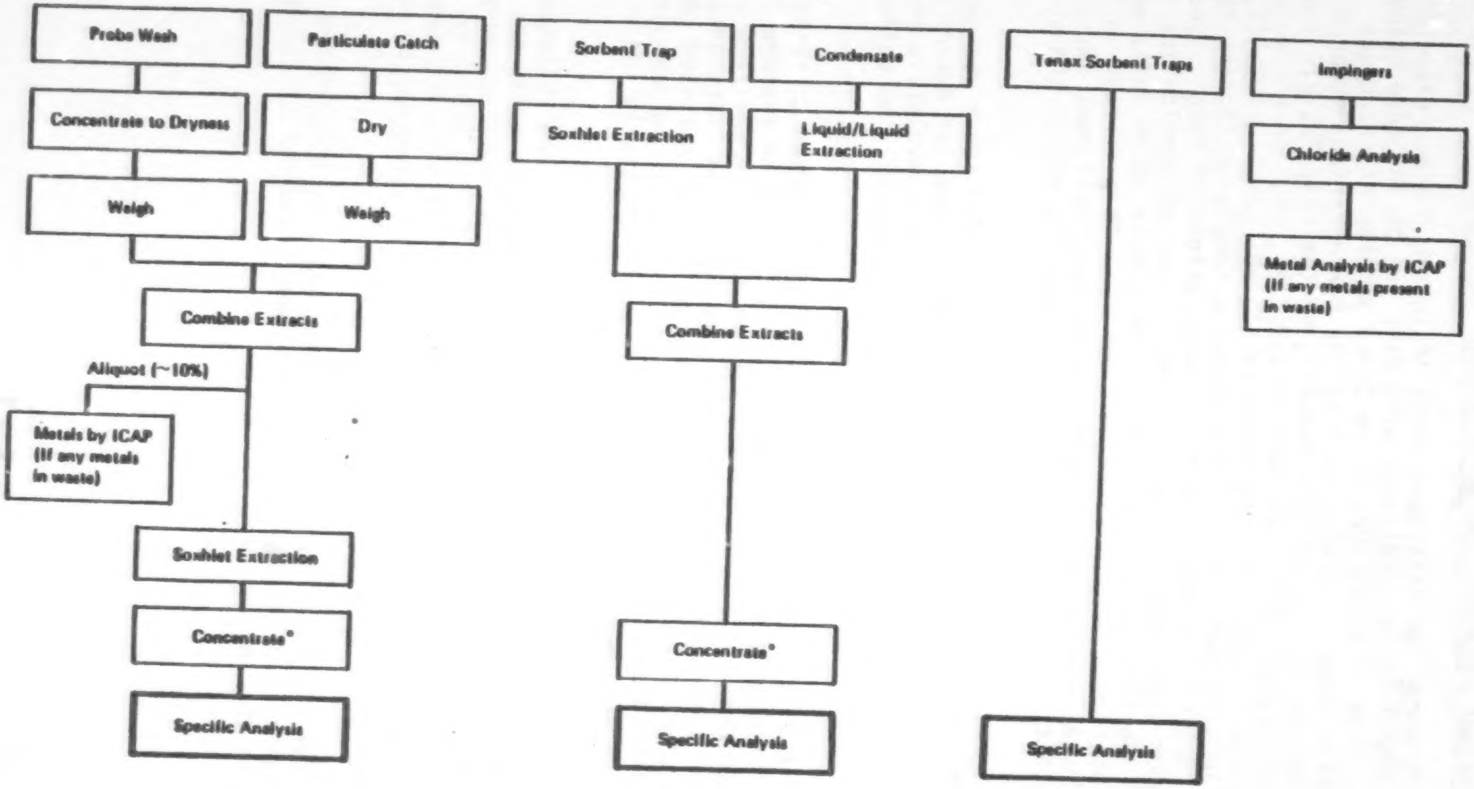
Probe Wash
Concentrate to Dryness
Weigh
Particulate Catch
Dry
Weigh
Combine Extracts
Aliquot (~10%)
Metals by ICAP (If any metals in waste)
Soxhlet Extraction
Concentrate*
Specific Analysis
Sorbent Trap
Soxhlet Extraction
Condensate
Liquid/Liquid Extraction
Combine Extracts
Concentrate*
Specific Analysis
Tenax Sorbent Traps
Specific Analysis
Impingers
Chloride Analysis
Metal Analysis by ICAP (If any metals present in waste)

Figure 3.3.3.3. Overview of an analysis scheme for stack gas samples from a comprehensive sampling train.

*As an alternative, the extracts from particulate and vapor portions of the train may be combined prior to analysis.

3.3.3.4 Additional Effluent Characterization Strategy

The basic strategy for sampling scrubber water, ash, and other residue (if any) is to prepare composite samples from grab subsamples, collected using the same types of sampling devices and tactics used for waste characterization. This sampling is required only during trial burns, in accordance with 40 CFR Part 122.27. These additional effluent samples are analyzed for POHCs to determine appropriate disposal or subsequent treatment methods and to ensure that significant discharges of POHCs in other media do not go undetected. A target detection limit of 0.01-0.5% of the mass feed rate of the POHC in the waste should be achievable with a reasonable sample size.

3.3.3.5 Selection of Specific Sampling and Analysis Methods

The preceding discussion has briefly described the RCRA regulations that define sampling and analysis requirements for hazardous waste incineration and presented an overview of the strategic sampling and analysis approaches that have been developed to meet these requirements. Section 3.3.4 (below) either will present descriptions of the specific sampling, sample preparation, and analysis methods that are recommended for implementation of this strategy (and which have not already been described in other sections of the manual) or will refer the user to the appropriate method or section.

This section will illustrate, by means of a hypothetical example, the transition from strategy, as described above, to methods as described below. The example is oversimplified in the interests of clarity, but should serve as a demonstration of how to develop and evaluate a hazardous waste incineration trial burn plan. The discussion will deal with sampling and analysis considerations only and will not address adequacy of design, operating conditions, or other engineering considerations.

Scenario

The owner/operator of an incineration facility seeks a RCRA permit to treat chlorinated organic waste material.

The facility is a liquid injection incinerator with a capacity of 10 x 10^6 Btu/hr; it is equipped with a wet scrubber for acid gas removal. A waste oil (less than 0.1% chlorine) is burned as auxiliary fuel. The proposed operating conditions for hazardous waste incineration include a combustion zone temperature of 2000° F (1100° C) and a residence time of 2 sec with 150% excess air.

The waste is a still bottom from the production of perchloroethylene. Based on engineering analysis it is expected to be a nonviscous organic liquid with a heating value greater than 5000 Btu/lb. The major components of the waste are expected to be highly chlorinated species such as hexachlorobenzene, hexachlorobutadiene, etc.

Strategy

It is hypothesized that there are insufficient data from other trial or operating burns to specify operating conditions under which this type of facility has been demonstrated to comply with the Part 264 performance criteria when burning this type of waste. Therefore, a trial burn will be required.

It is also hypothesized that there are data available from the waste generator which are sufficient to develop the trial burn plan. Therefore, additional analysis of the waste will not be necessary to support the trial burn permit application. The POHCs for which destruction and removal efficiencies are to be demonstrated in the trial burn must be designated, based on review of existing information and/or additional analysis of a representative sample of the waste.

Since the owner/operator plans to operate his facility under one set of temperature/residence time/excess air conditions when treating hazardous waste, the trial burn will consist of three replicate tests under that set of operating conditions.

The trial burn sampling and analysis strategy must address:

1. The waste analysis requirements of 40 CFR Part 122
2. The performance standards of 40 CFR Part 264 Subpart O
3. The monitoring requirements of 40 CFR Part 264 Subpart O

Sampling Strategy - During each of the three replicate tests the following samples must be obtained:

1. One composite sample of the waste actually treated
2. One time-averaged (3-4 hr) sample of stack gas
3. One composite sample of spent scrubber water

No bottom ash or fly ash streams (other than the stack particulate emissions) are expected to be generated as effluents from this facility.

Analysis Strategy - The waste must be analyzed to determine:

1. Quantity of designated trial burn POHCs
2. Heating value of the waste[a]
3. Viscosity or physical form[a]
4. Quantity of organically bound chlorine[a] (this analysis is not mandatory; however, the data obtained may be helpful in determining a potential for HCl emissions)
5. Identity and approximate quantity of known or suspected Appendix VIII constituents[a]

The stack gas must be analyzed to determine:

1. Quantity of designated trial burn POHCs
2. Quantity of particulate matter emissions
3. Quantity of hydrochloric acid emissions
4. Carbon monoxide level
5. Excess air level (oxygen/carbon dioxide level determination)

The scrubber water must be analyzed to determine quantities of designated trial burn POHCs.

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[a] It has been hypothesized for this example that this information was available from the waste generator. Some or all of these determinations may be repeated on the actual composite waste sample.

Tactics and Methods

Selection of POHCs - Table 3.3.3.5-1 summarizes the information that is hypothetically available from the generator of the waste in this example. The major organic components that would appear to be candidates for selection as POHCs are listed in Table 3.3.3.5-2, along with relevant physical/chemical properties are recommended stack sampling and analysis methods.

It is hypothesized that the permit writer has designated hexachlorobutadiene, hexachlorobenzene, and hexachloroethane as POHCs. All three species are present in significant concentrations in the waste and will remain at greater than 1000 mg/kg concentration even if the waste were cut by as much as 1:10 with auxiliary fuel in order to limit the total chlorine feed rate and to maintain an adequate heating value in the total incinerator feed. Fully chlorinated species such as these are generally considered to be highly resistant to thermal degradation and thus provide a set of "worst case" POHCs for DRE determination.

Selection of Sampling Methods - For sampling of wastes and liquid and solid effluents, the choice of method is based primarily on the nature of the medium. Review of available methods indicates that dipper (Section 1.2.1.3) or tap sampler techniques would be appropriate for collection of discrete subsamples of waste feed and of spent scrubber water at regular time intervals over the duration of each trial burn. These would then be combined to form the corresponding composite samples for each test.

For sampling of stack gas, both the nature of the medium and the nature (volatility, stability) of the POHC or other target species affects the choice of a sampling method. Table 3.3.3.5-2 (above) summarizes these recommendations for the candidate POHCs in this hypothetical example. Note that designation of tetrachloroethylene as a POHC in this instance would require use of VOST or gas bulb, while the Modified Method 5/SASS approach would collect all of the other candidate POHCs. The MM5 train would also suffice to determine compliance with the two other performance standards of 40 CFR Part 264. The particulate matter emission rate can be determined from the mass of material collected in the probe wash, cyclone (if any), and filter of the MM5 train prior to extraction for POHC analysis. The hydrochloric acid emission rate can be determined by using caustic scrubbing solution in the impinger portion of the MM5 train and determining the hydrochloric acid level as chloride.

In addition to the procedures chosen for the collection of POHCs, it would be necessary to specify procedures to accomplish the required monitoring for carbon monoxide and excess air (oxygen/carbon dioxide) levels in the stack gas.

Selection of Analysis Methods - The analytical procedures used for qualitative identification and quantitative determination of POHCs and other target species are determined primarily by the nature (volatility, polarity) of the species sought.

This manual lists recommended analysis methods for each candidate POHC after the appropriate sample preparation steps as described in Section 3.3.4 have been performed. Table 3.3.3.5-2 (above) summarizes the recommendation for analysis of the candidate POHCs in this hypothetical example. Note that

TABLE 3.3.3.5-1 AVAILABLE INFORMATION ON COMPOSITION OF HYPOTHETICAL WASTE

Visual Inspection: The waste was a pitch-black, nonviscous liquid with obvious particulate loading. It had a pungent odor and fumed slightly when the cap was removed.

Loss on Ignition: Ignition at 900° C resulted in a 99.8% loss of mass.

Higher Heating Value: The waste would not burn in a bomb calorimeter; its higher heating value is estimated at approximately 2000 Btu/lb.

Combustion Analysis: The waste was found to contain 21.35% C; 0.13% H; 0.07% N; 0.02% S; 74.42% Cl.

GC/MS: This analysis indicates that hexachlorobutadiene is the major component and hexachlorobenzene is present at about 10% of the C_4Cl_6 concentration. Other peaks in the chromatogram corresponded to hexachloroethane (approx. 4%), tetrachloroethanes (approx. 3%), tetrachloroethylene (approx. 0.1%), plus four others at about 0.5% concentration of the C_4Cl_6 concentration.

Summary: All of the available evidence suggests that this waste contains essentially no perchloroethylene, that hexachlorobutadiene makes up about 65% of the waste, and that there are perhaps a dozen other components at 1-5% concentration. All of the minor components appear to be chlorinated, with hexachlorobenzene the most abundant.

TABLE 3.3.3.5-2. CANDIDATE POHCs FOR HYPOTHETICAL WASTE AND RECOMMENDED STACK SAMPLING AND ANALYSIS METHODS FOR HYPOTHETICAL TRIAL BURN

Compound (POHC)	Approx. concentration in waste (%)	B.P. (°C)	ΔH[a] (kcal/mole)	MW (g/mole)	Stack sampling method		Analysis method	
					Section number	Description	Method number	Description
Hexachlorobutadiene	65	215	N/A	260.76	1.2.1.8[b]	MM5 - Sorbent	8120 or 8250	GC/MS Extractables
Hexachlorobenzene	6	323	567.7	284.8	1.2.1.8[b]	MM5 - Particulate and Sorbent	8120 or 8250	GC/MS Extractables
Hexachloroethane	2	186.8	173.8	236.74	1.2.1.8[b]	MM5 - Sorbent	8120 or 8250	GC/MS Extractables
Tetrachloroethane[c]	1.5	130.5 (146.2)	230 (233)	167.84	1.2.1.8[b]	MM5 - Sorbent	8010 or 8240	GC/MS Volatiles
Tetrachloroethylene	0.1	121.0	197	165.85	1.2.1.10	Gas Bulb Grab Sample or VOST	8010 or 8240	GC/MS Volatiles

[a] The Standard enthalpy of combustion.

[b] The SASS method (Section 1.2.1.9) could also be selected. A specially fabricated glass-lined SASS train might be necessary to withstand the hydrochloric acid expected in the stack.

[c] Numbers given in parentheses refer solely to 1,1,2-2-tetrachloroethane.

a single analytical method suffices to determine all of the hexachloro-species of concern here while an additional method would be recommended if it were desired to include the tetrachloroethanes and tetrachloroethylene.

Results and Calculations

This section illustrates the proper methods for calculating DRE, corrected particulate loading, and HCl emissions for the hypothetical example described above. Again, this example has been somewhat oversimplified for purposes of illustration.

According to 40 CFR Part 264, the DRE for each POHC is calculated as:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

where:

W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator

W_{out} = mass emission rate of the same POHC present in stack exhaust emissions.

Calculation of W_{in} (lb/hr) -

$$W_{in} = \frac{C_w \times FR_w}{100}$$

where:

C_w = Concentration of one POHC in the waste (%)

FR_w = Mass feed rate of waste to the incinerator (lb/hr).

Assume that quantitative analysis of a representative aliquot drawn from the composite waste sample from test No. 1 gave the following concentrations:

hexachlorobutadiene	63%
hexachlorobenzene	9.4%
hexachloroethane	1.1%

Further, assume that the 10 x 10^6 Btu/hr thermal capacity of the facility was met by blending waste 1:10 with waste oil, to give a feed mixture that was 7.5% chlorine and had a heating value of 16,400 Btu/lb. The total mass feed rate to the incinerator was therefore 600 lb/hr of which 540 lb/hr was auxiliary fuel (waste oil) and 60 lb/hr was chlorinated waste.

The W_{in} values for the three POHCs are therefore:

hexachlorobutadiene	(.63 x 60 lb/hr)	38 lb/hr
hexachlorobenzene	(.094 x 60 lb/hr)	5.6 lb/hr
hexachloroethane	(.011 x 60 lb/hr)	0.66 lb/hr

Calculation of W_{out} (lb/hr) -

$$W_{out} = C_s \times ER_s \times 1.32 \times 10^{-4}$$

where:

C_s = Concentration of one POHC in the stack gas effluent (mg/m^3)

ER_s = Volumetric flow rate of stack gas (m^3/min)

1.32 x 10^{-4} = Conversion factor from mg/min to lb/hr

Assume that quantitative analysis of the extract prepared from the time-integrated comprehensive sampling train sample from test No. 1 gave the following concentrations in the sampled gas:

hexachlorobutadiene	0.080 mg/m^3
hexachlorobenzene	0.020 mg/^{3}
hexachloroethane	$\leq$0.004 mg/m^3

Further, assume that the average measured volumetric flow of stack gas during test No. 1 was 3200 SCFM or 90 m^3/min.

The W_{out} values for the three POHCs are therefore:

hexachlorobutadiene	(.080 x 90 x 1.32 x 10^{-4})	9.5 x 10^{-4} lb/hr
hexachlorobenzene	(.020 x 90 x 1.32 x 10^{-4})	2.4 x 10^{-4} lb/hr
hexachloroethane	(<0.004 x 90 x 1.32 x 10^{-4})	<0.48 x 10^{-4} lb/hr

Calculation of DRE -

$$\mathrm{DRE} = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

The DRE values for the three POHCs are therefore:

hexachlorobutadiene	99.997
hexachlorobenzene	99.996
hexachloroethane	>99.993

Note that compliance with a "four-9's" performance standard could not have been demonstrated in this particular example for a component present at less than 1% in the waste itself (or less than 1000 mg/kg in the 1:10 waste: fuel blend fed to the incinerator) unless the detection limit for that component in the stack gas were less than 4 µg/m^3.

In this hypothetical example compliance with the 99.99% DRE performance standard has been demonstrated, in one test, for each of the three POHCs. If these results were supported by data from the other two replicate trial burn tests, the "four-9's" DRE could be considered to have been established.

Calculation of HCl Emissions - An incinerator burning highly chlorinated hazardous waste capable of producing significant stack gas emissions of hydrogen chloride (HCl) must monitor and/or control HCl emissions.

The hypothetical waste in this example contains approximately 75% chlorine by weight (Table 1). At the proposed 60-lb/hr feed rate of waste (blended 1:10 with auxiliary fuel for a total feed of 600 lb/hr or 9.8 x 10^6 Btu/hr), the maximum HCl emission rate would be 45 lb/hr of chlorine basis or 46 lb/hr as HCl. This is sufficiently high to warrant concern for potential HCl emissions and to indicate the necessity for stack measurement of HCl.

The stack emission rate of HCl can be calculated from:

$$\mathrm{HCl}_{out} = C_{in} \times ER_s \times 1.32 \times 10^{-4}$$

where:

C_{in} = Concentration of HCl (as Cl^-) in the stack gas effluent and collected in the impingers.

ER_s = Volumetric flow rate of the stack gas in m^3/min.

1.32×10^{-4} = Conversion factor from mg/min to lb/hr.

Assume that quantitative analysis of the impinger/condensate solution from the time-integrated comprehensive sampling train from test no. 1 gave 34 mg/m^3 HCl in the stack effluent.

The stack emission rate of HCl is calculated by:

$$HCl_{out} = 34 \text{ mg/m}^3 \ (90 \text{ m}^3\text{/min}) \ (1.32 \times 10^{-4})$$

$$= 0.40 \text{ lb/hr HCl}$$

This emission level is less than 1% of the 46 lb/hr of HCl potentially generated from the waste, indicating that the removal efficiency of the wet scrubber was greater than 99%.

Calculation of Particulate Loading (mg/m^3) - An incinerator burning hazardous waste must not emit particulate matter in excess of 180 milligrams per dry standard cubic meter when corrected to a standard excess air level in the stack gas.

Assume that prior to chemical analysis, particulate samples from the stack effluent of the hypothetical waste (from probe washes and filter catches of the time-integrated comprehensive sample train) were dried and weighed.

The hypothetical particulate loading from these measurements was calculated to be 80 mg/m^3 at the actual excess air level of the stack. The excess air level was determined to be 150% based on hypothetical measured values of oxygen (12.8%) and carbon dioxide (6.7%). Correction to standard excess air level as specified in the Part 264 regulations leads to a particulate loading of 140 mg/m^3 (0.06 gr/SCF). This total particulate emission is in compliance with the Part 264 performance standard that specifies less than or equal to 180 mg/m^3 (less than or equal to 0.08 gr/SCF).

Summary

It is apparent that this sample from the hypothetical waste when burned under these conditions complies with the Part 264 Subpart O Incinerator Standards as they relate to:

1. Destruction and Removal Efficiency. All three POHCs showed compliance with the 99.99% DRE performance standard.

2. Limitation on HCl Emissions. The HCl emission rate of 0.40 lb/hr shows compliance with a 99% removal standard for HCl.

3. Limitation on Stack Emissions of Particulate Material. The corrected particulate loading of 140 mg/m^3 shows compliance with the 180 mg/m^3 standard for particulate loading (corrected to a standard excess air level).

If these results are supported by data from two replicate hypothetical waste samples, compliance could be considered to have been established.

3.3.4 Sampling Methods

3.3.4.1 Overview

The sampling methods required for the ultimate analysis of POHCs in hazardous wastes and incinerator effluents during trial burns may need to address a variety of media. The hazardous waste prior to incineration may be in the form of a solid, liquid, slurry, or sludge. Following combustion, POHCs may be found in solids (e.g., bottom ash, fly ash/ESP catches), in liquids (scrubber water), or in the stack gas with its entrained particulate material. In this section, only brief descriptions of the sampling procedures are presented. Detailed sampling procedures are described in Section 1.4.

Liquid sampling methods and gaseous sampling methods are likely to be the most important methods for both routine monitoring and trial burn monitoring. It is expected that a majority of the hazardous wastes to be incinerated will be liquids, sludges, or slurries. Often these wastes will be contained in drums following transportation from the generator to the disposal facility. Such wastes are amenable to sampling with a Coliwasa. During trial burn situations, the calculation of the DRE value for the designated POHCs requires the measurement of those POHCs in the stack gas following all emission control devices. The required DRE value, 99.99% minimum, for POHCs places severe constraints on the sampling system for stack gases. It should be remembered that it is only during the trial burn that specific POHC sampling activity occurs. During routine incinerator operation, sampling requirements are significantly less. Samples generally need to be extracted or digested prior to analysis. Section Four of this manual provides necessary methods for sample preparation prior to analysis for all samples collected.

3.3.4.2 Sampling Methods for Influent Streams

The preferred sampling method for the influent streams to a hazardous waste incinerator depends upon the exact form of the influent (solid, sludge, liquid, etc.). Representative methods are described in Section 1.4.

3.3.4.3 Sampling Methods for Stack Gas

The sampling of stack gas components is most important to the hazardous waste incinerator permitting process. In general, the sampling apparatus for collecting stack gas effluents includes three major components: (1) an extractive probe which must be resistant to physical and chemical reactions with the gas being sampled, (2) one or more thermostatted compartments to maintain the gas at a temperature consistent with the collection medium (usually hot - 200° C - for particulate collection and cool - 20° C - for sorbent collection of volatile constituents), and (3) the sample collector. Some of the sampling devices integrate all three components into a single unit, while other methods require the addition of one or more components before they are suitable for use.

In general, the deployment of stack sampling trains for hazardous waste incinerator emissions measurements should parallel the procedures specified in EPA Methods 1-5 (see reference 3) for particulate emissions testing. Criteria selection of sampling port locations, number, location of sampling points within a stack and assurance of isokinetic sampling rates are comparable with an MM5 train and SASS and VOST trains. These criteria are discussed in both the specified EPA methods and in "Air Pollution (Volume III)" (see reference 4).

For specific information on available methods see Section 1.2. After collection, samples are prepared for analysis by methods given in Section Four of this manual.

3.3.4.4 Monitoring of Gaseous Combustion Products

As part of the routine documentation of the combustion performance of a hazardous waste incinerator, several parameters are monitored continuously in the incinerator stack. The primary component which needs to be monitored on a continuous basis or with high frequency (once per hour) is the level of carbon monoxide in the stack effluent. This measurement is needed during trial burns as well as during routine incinerator operation. Plume color and plume opacity may also be measured frequently for control purposes, although routine documentation is not required.

In addition, oxygen and/or carbon dioxide levels in the incinerator effluent must be measured to allow correction of the measured particulate loading to a standard excess air level. It may also be necessary in some cases to measure the incinerator effluent for hydrochloric acid for the purposes of calculating a removal efficiency.

Sample Conditioner

A portion of any on-line, continuous monitoring instrumentation setup for incinerator use is a sample delivery system which provides a properly conditioned representative sample to the instrumentation for measurement. The sample delivery system needs to include a sampling probe and a gas conditioner. For stack gas sampling, Pyrex glass or stainless steel probes may be used for the collection of particulates or gases. A gas conditioning process that will remove particulate and cool, dilute, or dehumidify the effluent is generally required prior to continuous analysis by instruments such as carbon dioxide monitors.

Carbon Monoxide Measurement

For measurement of the level of carbon monoxide in the incinerator effluent, a nondispersive infrared (NDIR) analyzer is recommended as the preferred analytical procedure (EPA Method 10; see reference 3). Selection of this instrument is consistent with the need to continuously monitor combustion efficiency by monitoring CO. Many commercial CO analyzers (NDIR) are available; however, selection should be based on the EPA specifications described in EPA Method 10 (reference 3). Such specifications are required to provide suitable quality control of the collected data by requiring that instrumentation meet certain criteria with regard to response time, span stability, and zero stability.

Plume Color and Plume Opacity

The color and opacity of the incinerator plume is best measured by EPA Method 9 (reference 3). EPA Method 9 involves the visual determination of plume opacity by a qualified observer. Commercially available smoke generators can be used to provide calibration of the observer during the certification procedures defined in EPA Method 9.

Oxygen/Carbon Dioxide Measurement

The oxygen/carbon dioxide levels in the incinerator effluent must be measured to allow correction of the measured particulate loading to a standard excess air level. EPA Method 3 (reference 3) involves the collection of a gas sample, and subsequent analysis of the oxygen level by an Orsat analyzer.

Hydrogen Halide Measurement

Several wet chemical methods are available for the measurement of hydrogen halides in stack gas effluents. These methods generally involve the collection of the hydrogen halides in impingers containing water or dilute alkali (0.2 N NaOH). A filter is utilized upstream of the impingers to remove particulates. Considering potential interferences, a specific ion electrode method is the preferred analysis method.

Recent research into the suitability of ion chromatography as a reliable tool for analysis of several anions corroborates the suitability of this technique for the analysis of hydrogen halides in stack gas samples. It is recommended that this technique, or the selective electrode technique, be used for the analysis of hydrogen halide in incinerator testing. Both techniques will permit analysis of effluent concentrations as low as about 1 ppm.

3.3.4.5 Sampling Methods for Solid and Liquid Effluents

The solid and liquid effluents from a hazardous waste incinerator, including bottom ash or fly ash/ESP catches, may be sampled by the methods discussed previously for the influent streams. Solid effluents will be sampled using scoops, corers, etc., as appropriate. Liquid effluents, primarily scrubber water, may be sampled by a variety of grab techniques including Coliwasa, dipper, and tap samplers.

3.3.5 References

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2. U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory. 1981. Engineering handbook for hazardous waste incineration. SW-889. Office of Environmental Engineering and Technology, Cincinnati, Ohio.

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4. Stern, A.C., ed. 1976. Air Pollution. Third edition, Vol. III. New York: Academic Press.

METHOD 1120

ELECTROCHEMICAL CORROSION METHOD

1.0 Introduction

1.1 Method 1120 is used to measure the corrosive properties of both aqueous and nonaqueous liquid wastes with respect to a standard steel.

1.2 This method is recommended for use only by or under the close supervision of analysts experienced in electrochemical corrosion measurements, the interpretation of polarograms, and detection of electrochemical interferences.

2.0 Summary of Method

2.1 An SAE Type 1020 coupon is prepared and secured in a corrosion cell. A polarization resistance measurement is performed by scanning through a potential range of ± 25 mV on either side of the corrosion potential. The slope of the polarization plot is then directly related to the corrosion rate.

3.0 Interference

3.1 The surface of the metal test coupon should be coated with ryton to reduce interference.

4.0 Apparatus and Materials

4.1 Scanning potentiostat having the ability to control an electrode potential within 1 mV of a preset value and measure a wide range of currents.

4.2 Potentiometer with a high impedance (10^{11} to 10^{14} Ω) and capable of detecting a change of 1.0 mV over a potential range between +4 V and -4 V.

4.3 Microammeter: Capable of measuring a current to within 1% of the absolute value over a current range between 1.0 and 10^6 µA.

4.4 Corrosion cell: Capable of accommodating the test coupon and containing working and reference electrodes and a thermometer.

4.5 Silicon carbide paper: 240 and 600 grit.

4.6 Micrometer: To be used to measure the dimensions of the test coupons.

4.7 SAE 1020 test coupons.

5.0 Reagents

5.1 Toluene: To be used for specimen preparation.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 No preservatives should be added to samples, since they may affect the sample's corrosive properties.

7.0 Procedure

7.1 Specimen preparation

7.1.1 Prepare the surface within 1 hr of the experiment. Wet grind with 240-grit SiC paper, wet polish with 600-grit SiC paper until previous coarse scratches are removed, rinse and dry.

7.1.2 Determine the surface area by measuring all dimensions to the nearest 0.01 mm. Subtract the area under any gaskets incorporated in the sample holder.

7.1.3 Clean the specimen just prior to immersion by degreasing for 5 min in boiling toluene or other suitable organic solvent (CAUTION: use under hood), followed by rinsing in distilled water.

7.1.4 If deemed necessary, the coupon can be further cleaned electrochemically in an acid electrolyte by evolving hydrogen at the specimen surface. This is accomplished by holding the specimen at a voltage 100 mV negative of the corrosion potential for approximately 1 min.

7.2 Measurement of corrosion potential

7.2.1 Set up the recorder and corrosion-measuring equipment in the Polarization Resistance mode according to the manufacturer's instructions.

7.2.2 Deaerate the solution thoroughly with an inert gas, such as nitrogen, to remove dissolved oxygen. After deaeration is complete (15-30 min), adjust the purge tube to provide a nitrogen blanket above the solution. Any gas bubbles adhering to the surface of the sample should be removed by wiping the surface with a lab tissue. The solution should be stirred magnetically during the Polarization Resistance determination. Isolate the cell so the solution temperature is not increased during the experiment by heat from the stirrer.

7.2.3 Measure the corrosion potential (E_{corr}) according to the manufacturer's instructions. Monitor the corrosion potential for several minutes to ensure a stable value. Adjust the instrument to apply an initial potential that is 20 mV negative of E_{corr}. Using a scan rate of 0.1 mV/sec, scan from the initial potential to a final potential that is 20 mV positive of E_{corr}.

7.2.4 The resulting current is plotted versus potential. The slope of the curve is related to the corrosion current by the following equation:

$$\Delta E/\Delta i = .022/i_{corr}$$

where:

$\Delta E/\Delta i$ = slope of the Polarization Resistance plot (ΔE in volts, Δi in microamps)

i_{corr} = corrosion current (μA).

Rearranging the above equation,

$$i_{corr} = 0.022\ (\Delta i/\Delta E)$$

The corrosion current can be related directly to the corrosion rate through the following equation:

$$\text{Corrosion rate (in milliinches per year)} = \frac{0.655\ i_{corr}\ (E.W.)}{d}$$

where:

E.W. = equivalent weight of the corroding species (g)

d = density of the corroding species (g/cm^3)

i_{corr} = corrosion current density (μA/cm^2).

7.3 The waste is determined to be corrosive if it has a corrosion rate greater than 0.250 in. (or 250 milliinches) per year. To facilitate the calculation of corrosion rates, an estimate for Tafel constants has been employed. Thus a safety factor of three has been included in the calculations. If desired, the analyst can obtain a more accurate corrosion rate by generating his own Tafel plots and calculating the anodic and cathodic Tafel constants.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 On a periodic basis, the analyst should employ ASTM Method G5-78 or G59-78 to check his experimental technique and instrumentation.

METHOD 1320

Multiple Extraction Procedure

1.0 Scope and Application

The Multiple Extraction Procedure (MEP) described in this method is designed to simulate the leaching a waste will undergo due to repetitive precipitation of acid rain on an improperly designed sanitary landfill. The repetitive extractions reveal the highest concentration of each constituent that is likely to leach in a natural environment. Method 1320 is applicable to liquid, solid, and miltiphasic samples.

2.0 Summary of Method

Waste samples are extracted according to the Extraction Procedure Toxicity Test (Method 1310) and analyzed for the constituents of concern listed in Table 1 using the 7,000 series methods. Then the samples are extracted nine (9) times using synthetic acid rain extraction fluid. If the concentration of any of the listed constituents of concern increases from the 7th or 8th extraction to the 9th extraction, the procedure is repeated until these concentrations decrease.

3.0 Interferences

Potential interferences that may be encountered during analysis are discussed in the individual methods referenced in Table 1.

4.0 Apparatus and Materials

4.1 Refer to Method 1310.

5.0 Reagents

5.1 Refer to Method 1310

5.2 Sulfuric Acid and Nitric Acid (60/40 weight percent mixture).

6.0 Sample Collection, Preservation and Handling

6.1 Refer to Method 1310

7.0 Procedure

7.1 Run the extraction procedure (EP) test in Method 1310.

7.2 Analyze the metals according to 7.18 of Method 1310.

7.3 Prepare a synthetic acid rain extraction fluid by adding the 60/40 weight percent sulfuric acid and nitric acid to distilled deionized water until the pH is 3.0 ± 0.2.

7.4 Take the solid phase of the sample remaining after the Separation Procedure of the Extraction Procedure and weight it. Measure an aliquot of synthetic acid rain extraction fluid equal to 20 times the weight of the solid sample. Do not allow the solid sample to dry before weighing.

7.5 Combine the solid phase sample and acid rain fluid in the same extractor as used in the EP, and begin agitation. Record the pH within 5-10 minutes after agitation has been started.

7.6 Agitate the mixture for 24 hours, maintaining the temperature at 20-40°C (68-104°F). Record the pH at the end of the 24 hour extraction period.

7.7 Repeat the Separation Procedure as described in Method 1310.

7.8 Analyze the extract for the constituents of concern listed in Table 1, using the same analytical methods as used for analyzing the EP extract.

7.9 Repeat steps 7.4 - 7.8 eight additional times.

7.10 If after completing the 9th synthetic rain extraction the concentration of any of the listed constituents of concern is increasing over that found in the 7th and 8th extractions, then continue extracting with synthetic acid rain until the concentration in the extract ceases to increase.

7.11 Report the initial and final pH of each extraction and the concentration of each listed constituent of concern in each extract.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures suggested in the referenced analytical methods should be followed.

METHOD 1330

EXTRACTION PROCEDURE FOR OILY WASTE

1.0 Scope and Application

1.1 Method 1330 is used to determine the mobile metal concentration (MMC) in oily wastes.

1.2 Method 1330 is applicable to API separator sludges, rag oils, slop oil emulsions and other oil wastes derived from petroleum refining.

2.0 Summary of Method

2.1 The sample is separated into solid and liquid components by filtration.

2.2 The solid phase is placed in a Soxhlet extractor, charged with tetrahydrofuran, and extracted. The THF is removed and the extractor is then charged with toluene and the sample is re-extracted.

2.3 The EP (Method 1310) is run on the dry solid residue.

2.4 The original liquid, combined extracts, and EP leachate are analyzed for the EP metals.

3.0 Interferences

3.1 Matrix interferences will be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste depending on the nature and diversity of the particular refinery waste being analyzed.

4.0 Apparatus and Materials

4.1 Soxhlet extraction apparatus

4.2 Vacuum pump or other source of vacuum

4.3 Buchner funnel 12

4.4 Electric heating mantle

4.5 Paper extraction thimble

4.6 Filter paper

4.7 Muslin cloth disks

4.8 Evaporative flask 250 ml

4.9 Analytical Balance capable of weighing to ± 0.5 mg.

5.0 Reagents

5.1 Tetrahydrofuran - ACS Reagent grade

5.2 Toluene

6.0 Sampling

6.1 Samples must be collected in glass containers having a total volume of at least 150 ml. No solid material should interfere with sealing the sample container.

6.2 Sampling devices should be wiped clean with paper towels or absorbent cloth and rinsed with a small amount of hexane followed by acetone rinse and dried between samples. Alternatively, samples can be taken with disposable sampling devices in beakers.

7.0 Procedure

7.1 Separate the sample (minimum 100 gm) into its solid and liquid components, using the filtration steps 7.1-7.6 in Method 1310.

7.2 Determine the quantity of liquid (ml) and the concentration of the metals of concern in the liquid phase (mg/l) using Method 3030, 3040, or 3050.

7.3 Place the solid phase into a Soxhlet extractor, charge the concentration flask with 300 ml tetrahydrofuran, and extract for three hours.

7.4 Remove the flask containing tetrahydrofuran and replace it with one containing 300 ml toluene.

7.5 Extract the solid for a second time, for three hours, with the toluene.

7.6 Combine the tetrahydrofuran and toluene extracts.

7.7 Determine the quantity of liquid (ml) and the concentration of the metals of concern in the combined extracts (mg/l) using either Method 3030 or 3040.

7.8 Take the solid material remaining in the Soxhlet thimble and dry it at 100°C for 30 minutes.

7.9 Run the EP (Method 1310) on the dried solid.

7.10 Calculate the mobil metal concentration (MMC in mg/l) using the following formula:

$$MMC = 1000\ ([Q_1 + Q_2 + Q_3]/[L_1 + L_2])$$

Q_1 = Amount of metal in initial liquid phase of sample (Amt. of Liquid X Conc. of Metal) (mg)

Q_2 = Amount of metal in combined organic extracts of sample (Amt. of

Q_3 = Amount of metal in EP Extract of solid (Amt. of extract X Conc. of Metal) (mg)

L_1 = Amount of Initial Liquid (ml)

L_2 = Amount of liquid in EP = weight of dried solid from step 9 x 20 (ml)

8.0 Quality Control

8.1 Standard quality assurance practices should be used with this method. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity accuracy of the analysis.

METHOD 3560

REVERSE PHASE CARTRIDGE EXTRACTION

1.0 Scope and Application

1.1 Method 3560 is designed to quantitatively extract non-purgeable organic compounds from groundwater samples using reverse phase concentration cartridges. This method is available as an alternative to Methods 3510, 3520, and 3530 for groundwater screening as described in Method 8600.

1.2 Method 3560 is advantageous compared to the other extraction methods since it is simple and effective and requires a minimum of sample preparation.

2.0 Summary of Method

2.1 The groundwater sample is drawn up into a 50-ml syringe and a pre-cleaned RP cartridge is fitted on the syringe. The sample is forced through the cartridge. This process is repeated with an additional 50 ml of sample.

2.2 The cartridge is washed with distilled water and then eluted either sequentially (for compound fractionation) or entirely with appropriate solvents.

3.0 Interferences

3.1 A procedural blank should be performed prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the sample.

4.0 Apparatus and Materials

4.1 Reverse phase C18 cartridges; (Water Sep Pac™, Analabs, or equivalent).

4.2 Glass Hypodermic Syringe; 50cc or larger.

4.3 Vials, 12 ml, borosolicate glass with Teflon Lined screw caps.

4.4 Distilled, deionized water.

4.5 Evaporation system (Pierce, Reacti-Therm™ system, or equivalent).

5.0 Reagents

5.1 Methanol: ACS reagent grade.

5.2 Hexane: ACS reagent grade.

6.0 Sample Collection, Preservation, Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation and handling.

6.2 After extraction of samples by this method, hexane and methanol extracts may be stored at 4°C prior to analysis. Sample extracts should be analyzed as soon as possible after extraction and should not exceed 4 weeks after extraction.

7.0 Procedure

7.1 Fill syringe with 5 ml methanol.

7.2 Attach reverse phase cartridge to the syringe and push the methanol through taking 1 min or more to completely empty the syringe.

7.3 Remove the cartridge and fill the syringe with 5 to 10 ml of distilled water.

7.4 Attach the cartridge and force the water through as before.

7.5 Remove the cartridge and fill the syringe with 50 ml of the sample groundwater.

7.6 Attach the cartridge and force the water sample through the cartridge at a rate of about 10 ml/min.

7.7 Repeat steps 7.5 and 7.6 with an additional 50 ml of sample.

7.8 Remove the cartridge and fill the syringe with 5 ml of distilled water. Attach the cartridge and force the distilled water through the cartridge as before.

7.9 Remove the cartridge and fill the syringe with 5-7 ml of hexane.

7.10 Attach the cartridge and force the hexane through 5 ml/min. Collect the hexane in a 12-ml vial.

7.11 At this point the sample volume should be reduced using an evaporation system that uses a stream of nitrogen and low heat (40-50°C). The sample volume should be reduced to ~.5 ml and made up to 1 ml with fresh hexane.

7.12 If the sample will not be analyzed immediately it should be sealed with a Teflon-lined cap and stored at 4°C until analysis.

7.13 Repeat steps 7.9 through 7.12 using methanol as the eluting solvent.

8.0 Quality Control

8.1 Every 10th sample or at least one sample in each set of samples should be a spiked duplicate. The sample should be spiked with 25 ng of fluoranthene, 0.4 µg of parathion and 0.4 µg of 2,4,5-trichlorophenol.

8.2 Every 10th sample or at least one sample in each set of samples should be a spiked reagent blank. A 100-ml sample of distilled water should be spiked with 25 ng of fluoranthene, 0.4 µg of parathion and 0.4 µg of 2,4,5-trichlorophenol.

8.3 A reagent blank (i.e., distilled deionized water) should be run with each set of samples. This blank will be used to determine whether interfering compounds have been introduced during sample preparation.

METHOD 3570

COLUMN CLEAN UP OF PETROLEUM WASTES

1.0 Scope and Application

1.1 Method 3570 is used to clean up samples containing high levels of aliphatic hydrocarbons, such as wastes from petroleum refining. This method is used specifically to separate aliphatics, aromatics, and polar compounds from the waste matrix.

1.2 Method 3570 is applicable to API separator sludges, rag oils, slop oil emulsion, and other oily wastes derived from petroleum refining.

1.3 Method 3570 is recommended for use only by, or under close supervision of, experienced residue analysts.

2.0 Summary of Method

2.1 A 10-ml extract or organic liquid waste is subjected to acid/base separation by Method 3530, followed by application to an alumina column of the base/neutral fraction. The column is then sequentially eluted with hexane, methylene chloride and methanol to obtain three fractions. Appropriate dilution factors for analysis are determined and the extracts are ready for analysis by Method 8270.

3.0 Interferences

3.1 Matrix interferences will likely be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste, depending on the nature and diversity of the particular waste being analyzed. However, a special caution is in order about water. The presence of water in the extract to be applied to the alumina column will adversely affect the column's sorption behavior. Thorough removal of water from the base/neutral extract is essential.

3.2 A second caution pertains to column loading. As the column loading for many of these wastes approaches 200 mg, separation recoveries will suffer. The use of additional clean-up extractions can be used, as necessary, for specific compound identification and quantitation.

4.0 Apparatus

4.1 Glass Column: 30 cm long x 1 cm I.D. with glass frit or glass wool and stop cock

4.2 Aluminum weighing boats: Approximately 2 in. in diameter

4.3 Analytical Balance: Capable of weighing to ± 0.5 mg

4.4 Concentrator Tube, KD, 10 ml

4.5 Evaporatove Flask, KD, 250 ml

4.6 Snyder Column, KD, Three-ball micro

4.7 Synder Column, KD, Two-ball micro

4.8 Steam Bath

4.9 Boiling Chips: 10-40 mesh carborundum. Heat to 450°C for 5-10 hours.

4.10 Syringe: 1 ml glass

4.11 50 ml beaker

4.12 250 ml beaker

4.13 Apparatus specified in Method 3530 of SW-846

5.0 Reagents

5.1 Hexane: Distilled in Glass (B&J) or equivalent

5.2 Methylene Chloride: Pesticide Quality or equivalent

5.3 Methanol: Distilled in Glass (B&J) or equivalent

5.4 Alumina: Dried overnight at 130°C, neutral 80-325 MCB chromatographic grade

5.5 Sodium Sulfate: (ACS) Granular anhydrous (purified by heating at 400°C for 4 hours in a shallow tray)

5.6 Sodium Hydroxide: (ACS) 10 N in distilled water

5.7 Sulfuric Acid: (1:1) Mix equal volumes of concentrated H_2SO_4 (ACS) with distilled water

6.0 Sample Collection, Perservation, and Handling

6.1 Samples are collected in glass containers having Teflon lined screw caps. Sampling devices should be wiped clean with paper towels or absorbant cloth and rinsed with a small amount of hexane, followed by acetone between samples. After rinsing, the sampling device should be wiped again with a clean towel or cloth and dried.

6.2 If samples require preservation they shoud be refrigerated at 4°C from the time of collection to extraction. API separator sludges, rag layers, etc., will generally not require preservation.

6.3 All samples should be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 A 10-ml aliquot of the liquid waste or waste extract is spiked with 500 ug each of d_9-acridine, d_5-nitrobenzene, 2-fluorobiphenyl tribromophenol, d_{14}-terphenyl, 2-fluorophenol, and d_{10}-pyrene in the separatory funnel of Method 3530/Step 7.1.

7.2 Method 3530 is executed on this mixture with the following modifications:

- In Step 7.3, filtration should not be used for emulsion breaking.
- In Step 7.6, both phases are worked up for analysis.
- The appropriate analytical solvent that is referenced for the base/neutral fraction is hexane, not methylene chloride.
- In Step 7.15, the base/neutral concentrate is not diluted to 10 mL with hexane. Rather, only enough hexane is added to solubilize the extract.

At this point, the acid extract is ready for analysis.

7.3 Weigh out 10.0 gm of alumina and add to the chromatograhic column that is filled to about 20 cm with hexane.

7.4 Allow the alumina to settle and then add .5 gm sodium sulfate.

7.5 Let the solvent flow such that the head of liquid in the column is about 1 cm above the sodium sulfate layer. Stop the flow.

7.6 Remove 100 uL of final base/neutral extract to a small tared vial.

7.7 Evaporate the hexane under a gentle stream of nitrogen.

7.8 Reweigh the vial to establish the number of mg of residue per mL of extract.

7.9 Spike a 100- to 200-mg equivalent aliquot of the base/neutral extract with 10 ug of d_5-phenol. Add this aliquot to the column.

7.10 Start the flow and elute with 13 ml of hexane. Collect the effluent in a 50 ml beaker. Label this fraction "base/neutral aliphatics".

7.11 Elute the column with 100 ml of methylene chloride and collect the effluent in a 250 beaker. Label "base/neutral aromatics".

7.12 Elute the column with 100 ml of methanol and collect the effluent in a 250 ml beaker. Label "base/neutral polars".

7.13 Weigh three aluminum sample boats to the nearest 0.5 mg. Reduce the volume of each fraction using the KDs to between 1 and 5 ml. Record the volume of each and place 1/2 of each sample in the respective boat.

7.14 Evaporate the liquid in each boat under a gentle stream of nitrogen. Reweigh each boat and record the weight of each fraction.

7.15 Calculate the weight of each fraction as a proportion of the total sample. For example fraction 1 is 56.3 mg, fraction 2 is 34.8 mg, and fraction 3 is 85.0 mg. The total weight applied was 273 mg.

Fraction 1	20.6
Fraction 2	12.7
Fraction 3	31.1
Unaccounted	35.6

7.16 Calculate the amount of sample in the fraction and adjust the sample volumes with the corresponding solvent so that injection will permit determination of various components on scale, but in no case should the amount of sample entering the column exceed 3 ug.

As an example, suppose that this step was performed on a waste and the obtained weight of the boat for fraction 1 was 28.3 mg, for fraction 2 was 12.7 mg, and for fraction 3 was 5.0 mg. Suppose further that 100-mg equivalent of waste was initially applied to the alumina column and that the volume of the unevaporatd liquid put in the fraction 2 boat was 2.5 ml. Then there are

$$12.7\text{mg}/2.5\text{ ml} = 5.1\text{ ug/ul}$$

in fraction 2. Consequently, fraction 2 should be diluted 1;1 with methylene chloride prior to entering the capillary column.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank sample should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis.

8.3 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.4 A rag oil sample was analyzed according to the procedure outlined in this method by a number of laboratories. The reconstructed ion chromatograms and target compound result are attached.

TABLE 3570 - 1

Standard Rag Oil

Selected Components

Constituent	Mean[a]	SD	R% SD
Naprthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	1614	296	18
2 Methyl-naphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methyl phenanthrene	2908	2014	69
Methyl dibenzothiophene	2200	1017	46

Average Surrogate Recoveries

Nitrobenzene - d_5	58.6	11
Terphenyl - d_{14}	83.0	2.6
Phenol - d_5	80.5	27.6
Napthalene - d_8	64.5	5.0

a/ Based on five determinations from 3 laboratories

Figure 3570-1

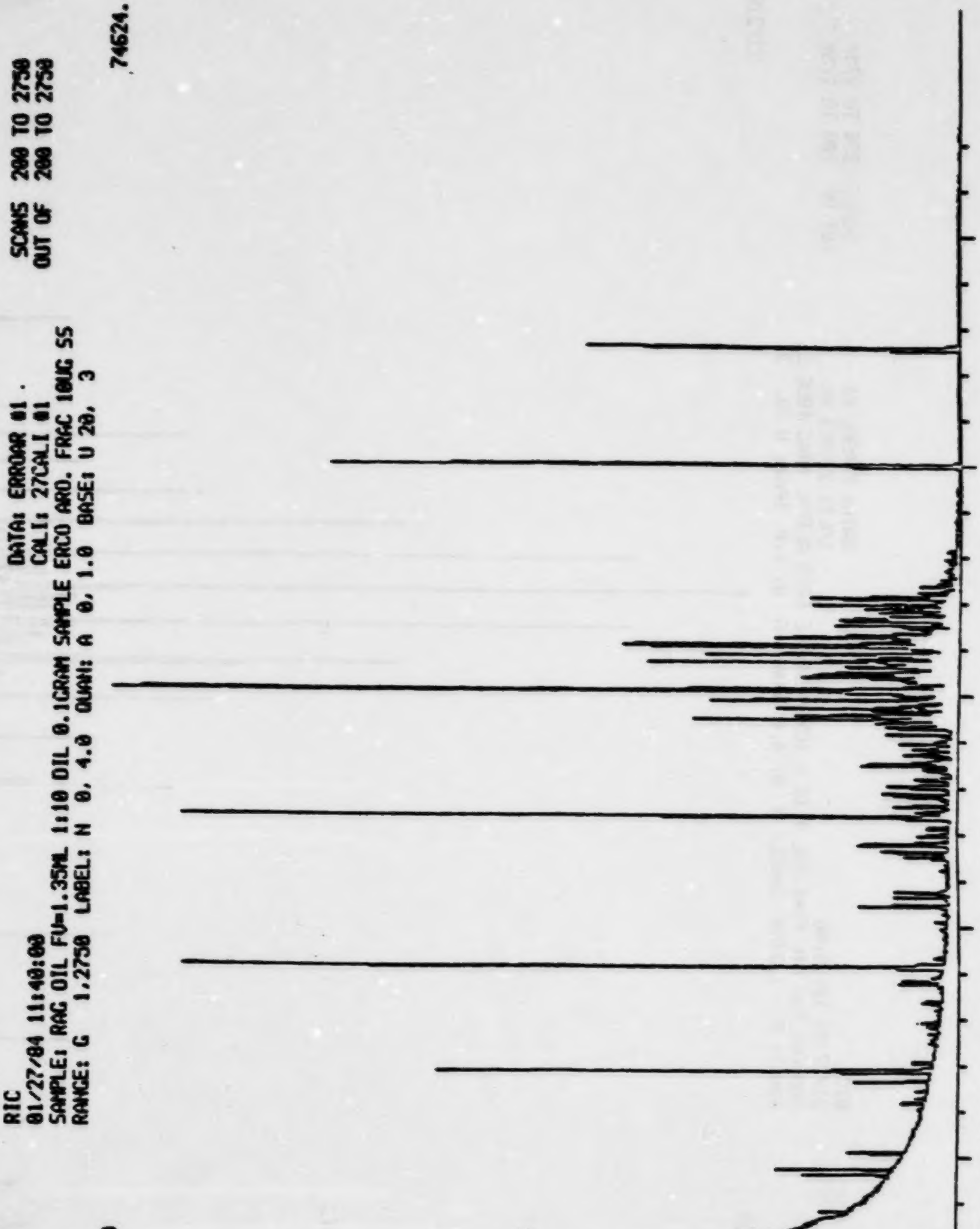
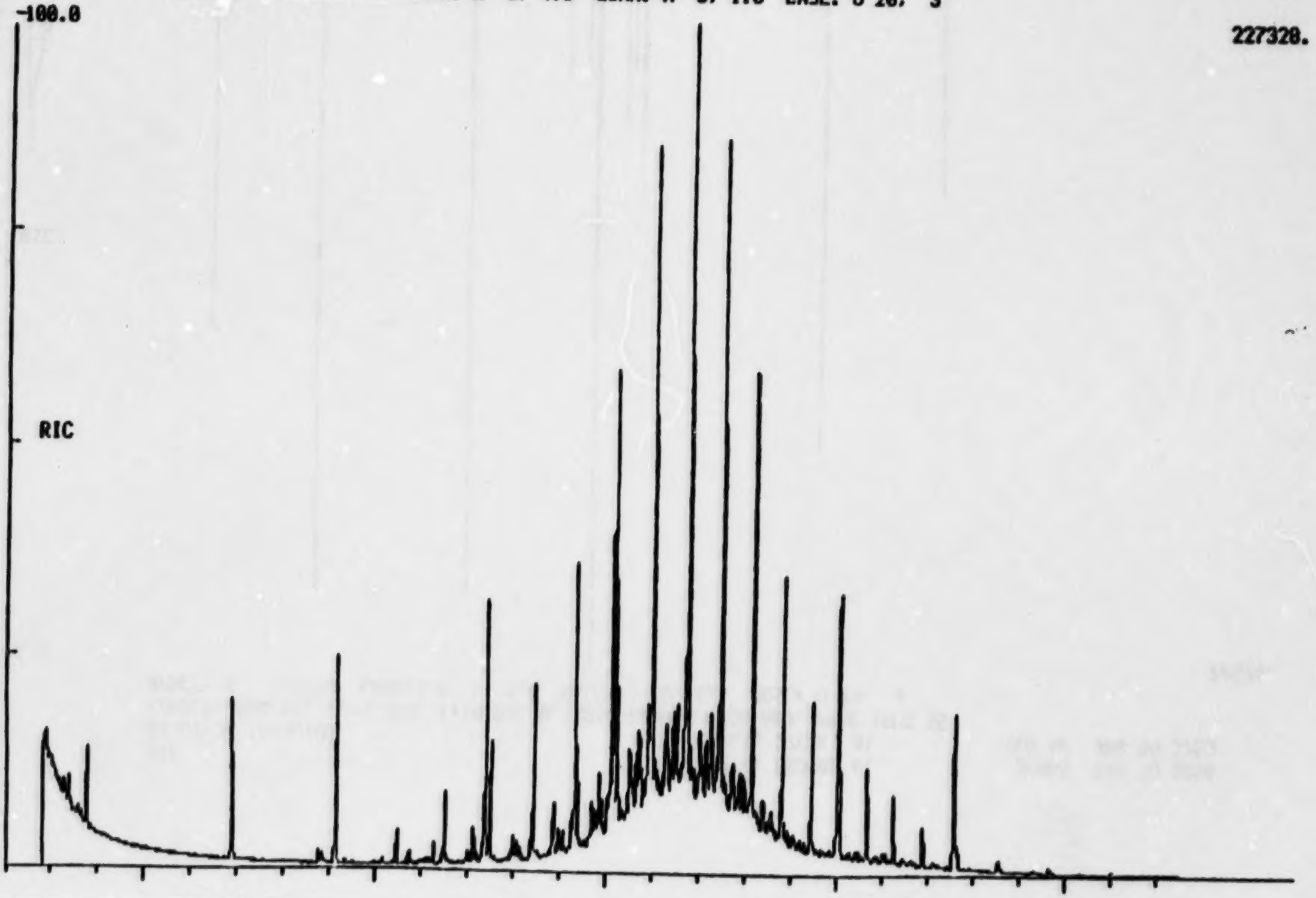


Figure 3570-2

RIC
01/27/84 12:36:00
SAMPLE: RAC OIL FV=1.9ML + IS 0.1GRAM SAMPLE ERCO ALIPH. FRAC 10UG SS
RANGE: G 1,2750 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

DATA: ERROAL 01
CALI: 27CALI 01

SCANS 200 TO 2750
OUT OF 200 TO 2750



METHOD 3720

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN

1.0 Scope and Applicability

1.1 This method covers the analysis of volatile POHCs collected on Tenax and Tenax/charcoal sorbent cartridges using a VOST. Much of the description for purge and trap GC/MS analysis is described in Methods 5030 and 8240 in this manual. Since the majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge and trap GC/MS. For the purposes of definition, volatile POHCs are those POHCs with boiling points less than 100°C.

1.2 This method is applicable to the analysis of Tenax and Tenax/charcoal cartridges used to collect volatile POHCs from wet stack gas effluents from hazardous waste incinerators.

1.3 The sensitivity of the analytical method for a particular volatile POHC depends on the level of interferences and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of the analytical method is 0.1 ng/l (20 ng on a single pair of traps) for a particular volatile POHC desorbed from either a single pair of Tenax and Tenax/charcoal cartridges or by thermal desorption of up to six pairs of traps onto a single pair of Tenax and Tenax/charcoal traps. The resulting single pair of traps are then thermally desorbed and analyzed by purge and trap GC/MS.

1.4 This method is recommended for use only by experienced analytical chemists or under the close supervision of such qualified persons.

2.0 Summary of Method

2.1 A schematic diagram of the analytical system is shown in Figure 1. The contents of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 minutes at 180°C with organic-free nitrogen gas (at a flow rate of 100 ml/min), bubbled through 5 ml of organic-free water, and trapped on an analytical absorbent trap. After the 10-minute desorption, the analytical adsorbent trap is rapidly heated to 180°C with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature programmed gas chromatography and detected by low resolution mass spectrometry. The concentrations of volatile POHCs are calculated using the internal standard technique.

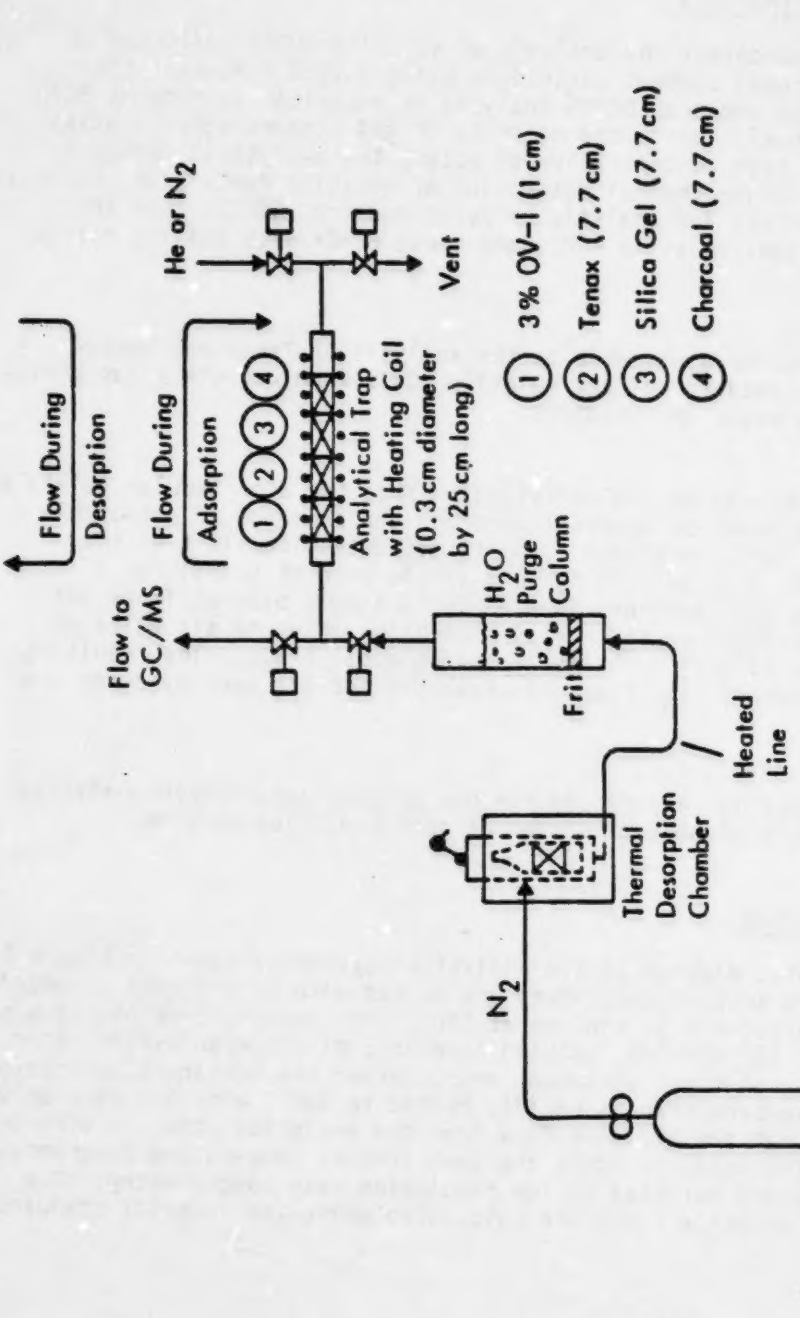

Flow to GC/MS
Flow During Desorption
Flow During Adsorption
He or N_2
Vent
① ② ③ ④
Analytical Trap with Heating Coil (0.3 cm diameter by 25 cm long)
H_2O Purge Column
Frit
Heated Line
Thermal Desorption Chamber
N_2
① 3% OV–1 (1 cm)
② Tenax (7.7 cm)
③ Silica Gel (7.7 cm)
④ Charcoal (7.7 cm)

Figure 1. Schematic diagram of trap desorption/analysis system.

3.0 Precision and Accuracy

3.1 The overall accuracy of sample collection and analysis using VOST has been determined in laboratory evaluations to be 50 to 150 percent for analysis of replicate traps (2). These values may be revised as further evaluation of VOST performance is conducted.

3.2 The precision for the internal standard response (area) should be 20 percent during any given analysis period at a particular multiplier voltage of the mass spectrometer.

4.0 Apparatus

4.1 Thermal Desorption Unit

4.1.1 The thermal desorption unit (Nutech Corporation Model 320 or equivalent) should be capable of thermally desorbing the sorbent resin tubes. It should be capable of heating the tubes to 180°C ±10°C with flow of organic-free nitrogen through the tubes.

4.2 Purge and Trap Unit

4.2.1 The purge and trap unit consists of three separate pieces of equipment: the sample purger, trap and the desorber. It should be capable of meeting all requirements of Method 5030 for analysis of purgeable organic compounds from water.

4.3 GC/MS System

As described in Section 4 of Method 8240.

5.0 Reagents

5.1 Water

5.1.1 Reagent water is defined as water in which an interferent is not observed at the detection limit of the parameters of interest.

5.1.2 Reagent water may be generated by passing tap water through a carbon filter bed containing about 450 grams of activated carbon (Calgon Corporation, Filtrasorb-300 or equivalent).

5.1.3 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.4 Reagent water may also be prepared by boiling distilled water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant free inert gas through the water for one hour. While still hot, the water should be transferred to a narrow mouth screw cap bottle and sealed with a Teflon lined septum and cap.

5.1.5 Other methods which can be shown to produce organic-free water can be used.

5.2 Analytical Trap Reagents

a) 2,6-diphenyline oxide polymer - Tenax (60/80 mesh) chromatographic grade or equivalent.

b) methyl silicone packing - 3% OV-1 on Chromosorb W (60/80 mesh) or equivalent.

c) silica gel, Davison Chemical (35/00 mesh), Grade 15 or equivalent.

d) charcoal, petroleum-based (SKC Lot 104 or equivalent) (see Section 6.2 in Part A); some users have found that improved performance can be obtained using only Tenax and charcoal in the analytical trap (2).

5.3 Stock Standard Solution

5.3.1 Stock standard solutions will be prepared from pure standard materials or purchased as certified solutions. The stock standards should be prepared in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.2 Fresh standards should be prepared weekly for volatile POHCs with boiling points of <35°C. All other standards must be replaced monthly or sooner if comparison with check standards indicates a problem.

5.4 Secondary Dilution Standards

5.4.1 Using stock standard solutions, prepare secondary dilution standards in methanol which contain the compounds of interest either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the desorbed calibration standards will bracket the working range of the analytical system.

5.5 Bromofluorobenzene (BFB) Standard

5.5.1 Prepare a 25 µg/ml solution of BFB in methanol.

5.6 Deuterated (d_6) Benzene

5.6.1 Prepare a 25 µg/ml solution in methanol.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Section 1.2.1.13 of this manual.

6.2 Sample trains obtained from the VOST should be analyzed within 2 weeks.

7.0 Procedures

7.1 Assembly of PTD Device

7.1.1 Assemble a purge and trap desorption device (P-T-D) which meets all the requirements of Method 5030 (Refer to Figure 1).

7.1.2 Connect the thermal desorption device to the purge and trap device. Calibrate the P-T-D - GC/MS system using the internal standard technique.

7.2 Internal Standard Calibration Procedure

7.2.1 This approach requires the use of deuterated benzene as the internal standard for these analyses. Other internal standards may be proposed for use in certain situations. The important criteria for choosing a particular compound as an internal standard are that it be similar in analytical behavior to the compounds of interest and it can be demonstrated that the measurement of the internal standard is not affected by method or matrix interferences. Other internal standards which have been used are d_{10}-ethylbenzene and d_4-1,2-dichloroethane. One user adds 50 ng of BFB to all sorbent cartridges (in addition to one or more internal standards) to provide continuous monitoring of the GC/MS performance relative to BFB.

7.2.2 Prepare calibration standards at a minimum of three concentration levels for each analyte of interest.

7.2.3 The calibration standards are prepared by spiking a blank Tenax or Tenax/charcoal trap with a methanolic solution of the calibration standards (including 50 ng of the internal standard, such as deuterated benzene) using the flash evaporation technique. The flash evaporation technique requires filling the needle of a 5.0 microliter (µl) syringe with clean methanol and drawing air into the syringe to the 1.0 µl mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25 µg/µl of the internal standard) to the 2.0 µl mark. The glass traps should be attached to the injection port of a gas chromatograph while maintaining the injector temperature at 160°C. The carrier gas flow through the traps should be maintained at about 50 ml/min.

7.2.4 After directing the gas flow through the trap, the contents of the syringe should be slowly expelled through the gas chromatograph injection port over about 15 seconds. After 25 seconds have elapsed, the gas flow through the trap should be shut off and the syringe removed, and the trap analyzed by the P-T-D - GC/MS procedure outlined in Section 10.2. The total flow of gas through the traps during addition of calibration standard to blank cartridges, or internal standards to sample cartridges, should be 25 ml or less.

7.2.5 Analyze each calibration standard for both Tenax and Tenax/charcoal cartridges according to Section 7.3. Tabulate the area response of the characteristic ions of each analyte against the concentration of the internal standard and calculate response factor (RF) for each compound using Equation 1.

$$RF = A_s C_{is} / A_{is} C_s$$

where A_s = Area of the characteristic ion for the analyte to be measured

A_{is} = Area of the characteristic ion for the internal standard

C_{is} = Amount (ng) of the internal standard

C_s = Amount (ng) of the volatile POHC in calibration standard

If the RF value over the working range is a constant (10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

7.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more of the calibration standards. If the response varies by more than ±25%, new calibration standards must be prepared and analyzed.

7.3 The schematic of the P-T-D - GC/MS system is shown in Figure 1. The sample cartridge is placed in the thermal desorption apparatus (Nutech 320 or equivalent) and desorbed in the P-T system by heating to 180°C for 10 minutes. The desorbed components pass into the bottom of the water column, are purged from the water and collected on the analytical adsorbent trap. After the 10-minute desorption period, the compounds are desorbed from the analytical adsorbent trap into the GC/MS system according to the procedures described in Method 8240.

7.4 Qualitative Identification

7.4.1 The procedure for qualitative identification of volatile POHCs using this protocol is described in Method 8240.

7.5 Calculations

7.5.1 When an analyte has been qualitatively identified, quantification should be based on the integrated abundance from the EICP of the primary characteristic ion chosen for that analyte. If the sample produces an interference for the primary characteristic ion, a secondary characteristic ion should be used.

7.5.1.1 Using the internal standard calibration procedure, the amount of analyte in the sample cartridge is calculated using the response factor (RF) determined in Section 7.2.5 and Equation 2.

$$\text{Amount of POHC} = A_s C_{is} / A_{is} RF \qquad (2)$$

where A_s = Area of the characteristic ion for the analyte to be measured

A_{is} = Area for the characteristic ion of the internal standard

C_{is} = Amount (ng) of internal standard

7.5.1.2 The choice of methods for evaluating data collected using VOST for incinerator trial burns is a regulatory decision. The procedures used extensively by one user are outlined below.

7.5.1.3 The total amount of the POHCs of interest collected on a pair of traps should be summed. These values should then be blank corrected. Guidelines for blank correction of sample cartridges are outlined below.

7.5.1.3.1 After all blanks (field and trip) are analyzed, a paired t-test should be used to determine whether trip blanks are significantly different from field blanks. If no difference is found, then the mean and standard deviation of the combined field and trip blanks for each POHC of interest is calculated.

7.5.1.3.2 If, using the paired t-test, the field and trip blanks are determined to be different, then the field blank (or the mean of multiple field blanks) associated with a particular run should be used as the blank value for that particular run.

7.5.1.4 Next, for each sample/POHC combination, a determination must be made as to whether a particular sample is significantly different from the associated blank. If the mean of the trip and field blanks is used, then a sample is different from the blank if:

(measured sample value) - (mean blank value) ≥3
x blank standard deviation

(If an individual field blank is used as the blank value, the above criteria do not apply.) If the sample is determined to be different from the blank according to the above criteria, then the emission value of a particular POHC is blank corrected by subtracting the mean blank value (as defined in Section 12.1.3) from the measured sample value.

7.5.1.5 If, according to the above procedures, the sample cannot be distinguished from the blank (i.e. for a given POHC there is a high sample value and high blank value or there is a low sample value and low blank value), the measured sample value is not blank corrected. In this case, the measured sample value is used to calculate a maximum emission value (and therefore a minimum DRE value) for that particular run.

7.5.1.6 The observation of high concentrations of POHCs of interest in blank cartridges indicates possible residual contamination of the sorbent cartridges prior to shipment to and use at the site. Data which fall in this category (especially data indicating high concentrations of POHCs in blank sorbent cartridges) should be qualified with regard to validity and blank data should be reported separately. The applicability of data of this type to the determination of DRE is a regulatory decision. Continued observation of high concentrations of POHCs in blank sorbent cartridges indicates that procedures for cleanup, monitoring, shipment and storage of sorbent cartridges by a particular user, be investigated to eliminate this problem.

7.5.1.7 If any internal standard recoveries fall outside the control limits established in Section 8.2.1, data for all analytes determined for that cartridge(s) must be qualified with the observation.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blank Tenax and Tenax/charcoal cartridges spiked with the analytes of interest. The laboratory is required to maintain performance records to define the quality of data which are generated. Ongoing performance checks must be compared with established performance criteria to determine if results are within the expected precision and accuracy limits of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 7.2.

8.1.2 The laboratory must spike all Tenax and Tenax/charcoal cartridges with the internal standard(s) to monitor continuing laboratory performance. This procedure is described in Section 7.2.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must spike blank Tenax and Tenax/charcoal with the analytes of interest at two concentrations in the working range.

8.2.1 The average response factor (R) and the standard deviation (S) for each must be calculated.

8.2.2 The average recovery and standard deviation must fall within the expected range for determination of volatile POHCs using this method. The expected range for recovery of volatile POHCs using this method is 50 to 150%.

8.3 The analyst must calculate method performance criteria for the internal standard(s).

8.3.1 Calculate upper and lower control limits for method performances using the average area response (A) and standard deviation(s) for internal standard:

Upper Control Limit (UCL) = A + 3S
Lower Control Limit (LCL) = A - 3S

The UCL and LCL can be used to construct control charts which are useful in observing trends in performance. The control limits must be replaced by method performance criteria as they become available from the USEPA.

8.4 The laboratory is required to spike all sample cartridges (Tenax and Tenax/charcoal) with internal standard.

8.5 Each day, the analyst must demonstrate through analysis of blank Tenax and Tenax/charcoal cartridges and reagent water that interferences from the analytical system are under control.

8.6 The daily GC/MS performance tests required for this method are described in Method 8240.

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3. FR, 44, 69464 (December 3, 1979); See also Method 624 for the Analysis of Purgeable Organics from Wastewater, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, July 1982.

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METHOD 6010

INDUCTIVELY COUPLED PLASMA METHOD

1.0 Scope and Application

1.1 Method 6010 is approved for determining the concentration of trace elements in mobility procedure extracts (exclusive of arsenic and selenium), wastes, and soils.

1.2 This method may be used for the determination of total elements in groundwater if the detection limit is less than primary interim drinking water standards or less than background levels.

1.3 All samples must be subjected to an appropriate dissolution step prior to analysis. (Refer to Section 2.1.)

1.4 Precaution must be taken to ensure that all spectral, chemical and physical interferences are detected and the appropriate corrective measures taken.

1.5 Use of this method is restricted to experienced spectroscopists.

1.6 Elements for which Method 6010 is an approved procedure are:

Aluminum
Antimony
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Molybdenum
Nickel
Potassium
Silica
Silver
Sodium
Thallium
Vanadium
Zinc

2.0 Summary of Method

2.1 Prior to analysis by Method 6010, samples must be prepared for sample introduction. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge-type samples are prepared using the procedure described in Method 3050. For samples containing oils, greases or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Method 6010 describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma

(ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 3.1 (and tests for their presence as described in 3.2) should also be recognized and appropriate corrections made.

3.0 Interferences

3.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

3.1.1 Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference for an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for indicating potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1.1 The interference information, which was collected at the Ames Laboratory,[1] is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/liter of the interference element. The suggested use of this

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[1] Ames Laboratory, U.S. DOE, Iowa State University, Ames, Iowa 50011.

TABLE 1. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated detection limit[b] (μg/l)
Aluminum	308.215	45
Arsenic	193.696	53[c]
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see[d]
Selenium	196.026	75[c]
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see 3.1.1). In time, other elements may be added as more information becomes available and as required.

[b] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample-dependent and may vary as the sample matrix varies.

[c] Method may not be applicable for groundwater analysis for these metals.

[d] Highly dependent on operating conditions and plasma position.

TABLE 2. ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

		Interferent (mg/l)									
Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/liter of aluminum. According to Table 2, 100 mg/liter of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/liter. Therefore, 10 mg/liter of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/liter. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

3.1.1.2 Only those interferents listed were investigated, and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

3.1.1.3 At present, information on the listed silver and potassium wavelengths is not available but it has been reported that second order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by diluting the sample and/or utilizing standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate, causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, the use of a high solid nebulizer can reduce salt build-up in the nebulizer and can also prevent drifting and loss of sensitivity in the instrument. In addition, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

3.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique; however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	mg/liter	Interferents	mg/liter
Al	10	Al	1,000
As	10	Ca	1,000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1,000
Ca	1	Mg	1,000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

3.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 3.2.1 through 3.2.4, will ensure the analyst that neither positive nor negative interferences will have on any of the analyte elements and distort the accuracy of the reported values.

3.2.1 Serial dilution: If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

3.2.2 Spike addition: A spike addition added at a minimum level of 10x the instrumental detection limit (maximum 100x) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect. CAUTION: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (see 3.2.3).

3.2.3 Comparison with alternate method of analysis: When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry or other approved methodology.

3.2.4 Wavelength scanning of analyte line region: If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

4.0 Apparatus and Materials

4.1 Inductively coupled plasma-atomic emission spectrometer

4.1.1 Computer-controlled atomic emission spectrometer with background correction.

4.1.2 Radiofrequency generator.

4.1.3 Argon gas supply, welding grade or better.

4.2 Operating conditions: Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst (1) to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and (2) to maintain quality control data confirming instrument performance and analytical results.

5.0 Reagents

5.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

5.1.1 Acetic acid, conc.

5.1.2 Hydrochloric acid, conc.

5.1.3 Hydrochloric acid (1:1): Add 500 ml conc. HCl to 400 ml Type II water and dilute to 1 liter.

5.1.4 Nitric acid, conc.

5.1.5 Nitric acid (1:1): Add 500 ml conc. HNO_3 to 400 ml Type II water and dilute to 1 liter.

5.2 Type II water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use Type II water for the preparation of all reagents, calibration standards, and as dilution water. The purity of this water must be equivalent to or better than ASTM Type II reagent water of Specification D1193.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hr at 105° C unless otherwise specified. (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow.

5.3.1 Aluminum solution, stock, 1 ml=100 µg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 ml of (1:1) HCl and 1 ml of conc. HNO_3 in a beaker. Warm gently to dissolve. When solution is complete, transfer quantitatively to a one liter flask and add an additional 10 ml of (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.2 Antimony solution, stock, 1 ml=100 µg Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in Type II water, add 10 ml (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.3 Arsenic solution, stock, 1 ml=100 µg As: Dissolve 0.1320 g of As_2O_3 in 100 ml of Type II water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.4 Barium solution, stock, 1 ml=100 µg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250° C for 2 hr) in 10 ml Type II water with 1 ml (1:1) HCl. Add 10.0 ml (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.5 Beryllium solution, stock, 1 ml=100 µg Be: Do not dry. Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ in Type II water, add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.6 Boron solution, stock, 1 ml=100 µg B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in Type II water and dilute to 1,000 ml. Keep in a tightly stoppered bottle, and store in a desiccator to prevent the entrance of atmospheric moisture.

5.3.7 Cadmium solution, stock, 1 ml=100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.8 Calcium solution, stock, 1 ml=100 µg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180° C for 1 hr before weighing in Type II water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.9 Chromium solution, stock, 1 ml=100 µg Cr: Dissolve 0.1923 g CrO_3 in Type II water. When solution is complete, acidify with 10 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.10 Cobalt solution, stock, 1 ml=100 µg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1:1) HNO_3. Add 10.0 ml (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.11 Copper solution, stock, 1 ml = 100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

5.3.12 Iron solution, stock, 1 ml=100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 ml (1:1) HCl and 2 ml of conc. HNO_3. Cool, add an additional 5.0 ml of conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.13 Lead solution, stock, 1 ml=100 µg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1:1) HNO_3. Add 10.0 ml (1:1) HNO_3 and dilute to 1,000 ml with Type II water.

5.3.14 Magnesium solution, stock, 1 ml=100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1:1) HNO_3. Add 10.0 ml (1:1) conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.15 Manganese solution, stock, 1 ml=100 µg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture (10 ml conc. HCl and 1 ml conc. HNO_3) and dilute to 1,000 ml with Type II water.

5.3.16 Molybdenum solution, stock, 1 ml=100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in Type II water and dilute to 1,000 ml with Type II water.

5.3.17 Nickel solution, stock, 1 ml=100 µg Ni: Dissolve 0.1000 g of nickel metal in 10.0 ml hot conc. HNO_3, cool, and dilute to 1,000 ml with Type II water.

5.3.18 Potassium solution, stock, 1 ml=100 µg K: Dissolve 0.1907 g KCl, dried at 110° C, in Type II water and dilute to 1,000 ml.

5.3.19 Selenium solution, stock, 1 ml=100 µg Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 in Type II water and dilute to 1,000 ml.

5.3.20 Silica solution, stock, 1 ml=100 µg SiO_2: Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in Type II water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.21 Silver solution, stock, 1 ml=100 µg Ag: Dissolve 0.1575 g $AgNO_3$ in Type II water and 10 ml conc. HNO_3. Dilute to 1,000 ml with Type II water.

5.3.22 Sodium solution, stock, 1 ml=100 µg Na: Dissolve 0.2542 g NaCl in Type II water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.23 Thallium solution, stock, 1 ml=100 µg Tl: Dissolve 0.1303 g $TlNO_3$ in Type II water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.24 Vanadium solution, stock, 1 ml=100 µg V: Dissolve 0.2297 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.25 Zinc solution, stock, 1 ml=100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.4 Mixed calibration standard solutions: Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see 5.4.1 through 5.4.5). Add 2 ml of (1:1) HNO_3 and 10 ml of (1:1) HCl and dilute to 100 ml with Type II water (see Note 1 in Section 5.4.5 and Note 6 in Section 7.3). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements be compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see 5.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

5.4.1 Mixed standard solution I: Manganese, beryllium, cadmium, lead, and zinc.

5.4.2 Mixed standard solution II: Barium, copper, iron, vanadium, and cobalt.

5.4.3 Mixed standard solution III: Molybdenum, silica, arsenic, and selenium.

5.4.4 Mixed standard solution IV: Calcium, sodium, potassium, aluminum, chromium, and nickel.

5.4.5 Mixed standard solution V: Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 ml of Type II water and warm the flask until the solution clears. Cool and dilute to 100 ml with Type II water. For this acid combination, the silver concentration should be limited to 2 mg/l. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve while the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by diluting 2 ml of (1:1) HNO_3 and 10 ml of (1:1) HCl to 100 ml with Type II water (see Note 6 in Section 7.3). Prepare a sufficient quantity to be used to flush the system between standards and samples.

5.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 Standards: In addition to the calibration standards, an instrument check standard, an interference check sample, and a quality control sample are also required for the analyses.

5.6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves (see 8.5.1).

5.6.2 The interference check is prepared by the analyst in the following manner. Select a representative sample that contains minimal concentrations of the analytes of interest but known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/liter or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati.

5.6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/liter and in accordance with the instructions provided by the supplier.

6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Samples containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene, or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; and rinsed with (1:1) nitric acid, tap water, (1:1) hydrochloric acid, tap water, and finally Type II water, in that order (see Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. The use of chromic acid can cause a contamination problem for the determination of chromium if the glassware is not rinsed properly. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick Street, New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

6.3 Aqueous samples must be preserved and pretreated appropriately depending on whether data on dissolved, suspended, or total metals are desired.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 The following definitions are intended to clarify the ensuing discussion.

7.1.1 Instrumental detection limit: The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of twenty replicate measurements of a reagent blank signal at the same wavelength.

7.1.2 Sensitivity: The slope of the analytical curve, i.e., functional relationship between emission intensity and concentration.

7.1.3 Instrument check standard: A multielement standard of known concentration prepared by the analyst to monitor and verify instrument performance on a daily basis (see 5.6.1).

7.1.4 Interference check sample: A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors (see 5.6.2).

7.1.5 Quality control sample: A solution obtained from an outside source having known concentration values to be used to verify the calibration standards (see 5.6.3).

7.1.6 Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the the analytical curve; see 5.4).

7.1.7 Linear dynamic range: The concentration range over which the analytical curve remains linear.

7.1.8 Reagent blank: A volume of Type II water containing the same acid matrix as the calibration standards carried through the entire analytical scheme (see 5.5.2).

7.1.9 Calibration blank: A volume of Type II water acidified with HNO_3 and HCl (see 5.5.1).

7.1.10 Method of standard addition: The standard addition technique involves the use of the unknown and unknown plus a known amount of standard (see 7.9.1).

7.2 Sample preparation: Aqueous samples should be prepared according to Section 7.3. Sludge-type samples should be prepared according to Method 3050 and samples containing oils, greases, or waxes may be prepared according to Methods 3030 and 3040. The applicability of a sample preparative technique to a new matrix type must be demonstrated by analyzing spiked sample or relevant standard reference materials.

7.3 Preparation of aqueous samples: For the determination of total elements, choose a measured volume of the well-mixed acid-preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker (see note 5 below). Add 3 ml conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5-ml portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add 10 ml of (1:1) HCl and 15 ml of Type II water per 100 ml final solution and warm the beaker gently for 15 min to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with Type II water and filter the sample to remove insoluble material that could clog the nebulizer (see Note 4 below). Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (see Note 6 below). Concentrations so determined shall be reported as "total."

NOTE 4: In place of filtering, after diluting and mixing, the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

NOTE 5: If low determinations of boron are critical, quartz or polypropylene glassware should be used. Polypropylene glassware is generally preferred since it is cheaper and just as accurate as quartz.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in 7.3, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

7.4 Set up instrument with proper operating parameters established in Section 4.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min of operation prior to calibration.

7.5 Initiate appropriate operating configuration of computer.

7.6 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (5.5.1) between each standard (see Note 7 below). (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 µg/liter extended flush times of 1 to 2 min may be required.

7.7 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits, whichever is lower). If they do, follow the recommendations fo the instrument manufacturer to correct for this condition.

7.8 Begin the sample run by flushing the system with the calibration blank solution (5.5.1) between each sample (see Note 7). Analyze the instrument check standard (5.6.1) and the calibration blank (5.5.1) after each 10 samples.

7.9 If it has been found that methods of standard addition are required, the following procedure is recommended.

7.9.1 The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B)\, V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration.

1. The analytical response signals must be linear with respect to concentration.

2. The chemical form of the analyte added must respond the same as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

7.10 Calculations: Reagent blanks (5.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion. If dilutions were performed, the appropriate factor must be applied to sample values. All results should be reported in mg/liter with up to three significant figures.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute samples if they are more concentrated that the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one procedural blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 Check the instrument standardization by analyzing appropriate quality control check standards as follows:

8.5.1 Analyze an appropriate instrument check standard (5.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ±5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

8.5.2 Analyze the calibration blank (5.5.1) at a frequency of 10%. The result should be within the established control limits of 2 standard deviations of the mean value. if not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem, and recalibrate the instrument.

8.5.3 To verify interelement and background correction factors, analyze the interference check sample (5.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.5.4 A quality control sample (5.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within ±5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

8.6 Spiked samples or standard reference materials shall be employed periodically to ensure that correct procedures are being followed and that all equipment is operating properly.

8.7 The method of standard additions shall be used for the analysis of all EP extracts and whenever a sample suffers from matrix interferences.

8.8 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.9 In an EPA round-robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

	Sample #1			Sample #2			Sample #3		
Element	True value (µg/l)	Mean reported value (µg/l)	Mean standard deviation (%)	True value (µg/l)	Mean reported value (µg/l)	Mean standard deviation (%)	True value (µg/l)	Mean reported value (µg/l)	Mean standard deviation (%)1
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

[a] Not all elements were analyzed by all laboratories.

METHOD 7090

BERYLLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7090 is an atomic absorption procedure approved for determining the concentration of beryllium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7090, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an acetylene/nitrous oxide flame. The resulting absorption of hollow cathode radiation will be proportional to the beryllium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.002 mg/l; typical sensitivity is 0.025 mg/l for 1% absorption.

3.0 Interferences

3.1 Background correction may be required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Concentrations of aluminum greater than 500 ppm may suppress beryllium absorbance. The addition of 0.1% fluoride has been found effective in eliminating this interference. High concentrations of magnesium and silicon cause similar problems requiring the use of the method of standard additions.

3.3 Enhancement is caused by excess of the following acids: nitric (>10 mg/ml), sulfuric (>1), phosphoric (>10), Fluoroboric, and acetic. Enhancement is also caused by many metals. Therefore, the addition of 10 mg/ml is recommended.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate. The method of standard additions should be used to correct the problem.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Beryllium hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Beryllium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. J. Booker or Fisher Scientific) and verify by comparison with a second standard, or dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 ml nitric acid and dilute to 1 liter. Beryllium metal can also be idssolvd in HCC.

5.4 Beryllium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

5.7 Cylinders
of nitrous oxide suitable for instrumental analysis.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic or glass containers are suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. If dissolved metal content is to be determined, filtering of the sample preferably in the field, must take place prior to acidification.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 234.9-nm wavelength line and background correction shall be used.

7.3 Fuel-rich nitrous oxide/acetylene shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of beryllium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 10 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7091

BERYLLIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7091 is an atomic absorption procedure approved for determining the concentration of beryllium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7091, samples must be prepared in order to convert organic forms of beryllium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the beryllium concentration.

2.3 The typical detection limit for this method is 0.2 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, beryllium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Calcium has been observed to suppress the Be signal. A 5% solution of H_2SO_4 was found to overcome this suppression.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Beryllium hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Beryllium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. T. Baker,or Fisher Scientific) and verify by comparison with a second standard, or dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 ml concentrated nitric acid and dilute to 1 liter. Beryllium metal can also be dissolved in HLC.

5.4 Beryllium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. If dissolved metal contact is to be determined, filtering of the sample, preferably in the field, must take place prior to acidification.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 234.9-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of beryllium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7198

HEXAVALENT CHROMIUM: DIFFERENTIAL PULSE POLAROGRAPHY

1.0 Scope and Application

1.1 This method is used to determine the concentration of hexavalent chromium in natural and waste waters and in EP extracts.

1.2 The method can quantitate chromium in concentrations of up to 1.0 mg/l to 5.0 mg/l depending on the mercury drop size. Higher concentrations can be determined by dilution.

1.3 The lower limit of detection for hexavalent chromium is 10 µg/l for the instrumental conditions given in this method. The limit of detection could be easily lowered by changing these conditions.

2.0 Summary of Method

2.1 Method 7198 measures the peak current produced from the reduction of hexavalent chromium to trivalent chromium at a dropping mercury electrode during a differential pulse voltage ramp.

2.2 The method described herein utilizes 0.125 M NH_4OH-0.125 M NH_4Cl as the supporting electrolyte. In this electrolyte, hexavalent chromium reduction results in peak current occurring at the peak potential (E_p) of -0.250 V vs. Ag/AgCl.

2.3 Alternative supporting electrolytes, such as those given in Table 1, may be used.

2.4 The technique of standard additions must be used to quantitate the hexavalent chromium content.

3.0 Interferences

3.1 Copper ion at concentrations higher than the hexavalent chromium concentration is a potential interference due to peak overlap when using the 0.125 M ammonical electrolyte. Increasing the ammonical electrolyte concentration to 0.5 M shifts the copper peak cathodically (E_p = -0.4 V), eliminating the interference at a copper-to-chromium ratio of 10:1 (Figure 1).

3.2 Reductants such as ferrous iron, sulfite, and sulfide will reduce hexavalent chromium to trivalent chromium; thus it is imperative to analyze the samples as soon as possible.

TABLE 1. POLAROGRAPHY OF HEXAVALENT CHROMIUM

Supporting electrolyte	Peak potential (vs. SCE)
1 M NaOH	-0.85
1 M Pyridine, 1 M NaOH	-1.48
1 M NaOH, 1 M NH_4Cl	-0.36
0.1 M NH_4OH, 0.1 M $(NH_4)_2$ Tartrate	-0.244
0.2 M KCl, 0.3 M Triethanolamine, pH 9	-0.28
1 M Na_2SO_4	-0.23
0.1 M NH_4OH, 0.1 M NH_4Cl	-0.25

4.0 Apparatus and Materials

4.1 Polarographic instrumentation capable of performing differential pulse analyses including recorder or plotter.

4.2 Dropping mercury electrode assembly capable of performing differential pulse analyses.

4.3 Counter electrode, platinum wire.

4.4 Reference electrode, Ag/AgCl or SCE, with a slow leakage fritted tip (unfired Vycor^R).

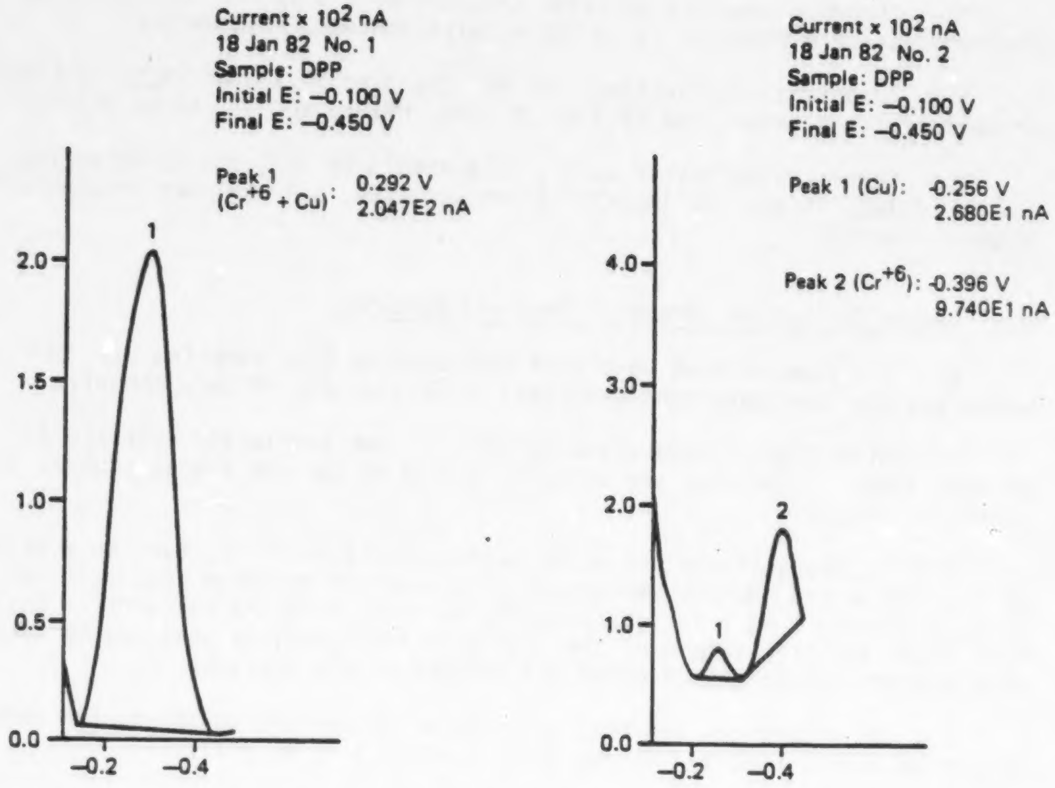
4.5 Nitrogen gas and cell outgassing assembly.

4.6 Micropipets and disposable tips.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Chromium standard solution I, 1.0 ml = 100 µg Cr: Should be made daily from a 1,000-ppm standard stock solution.



A. 20 ppm Cu, 2.5 ppm Cr, 0.1 N buffer.

B. 20 ppm Cu, 2.5 ppm Cr, 0.5 N buffer.

Figure 1. Two polarograms illustrating shift in copper peak at higher ammoniacal electrolyte concentrations.

5.3 Chromium standard solution II, 1.0 ml = 10 µg Cr: Should be made daily from a 1,000-ppm standard stock solution.

5.4 Chromium standard solution III, 1.0 ml = 1 µg Cr: Dilute 10 ml chromium standard solution II to 100 ml with demineralized water.

5.5 Ammoniacal electrolyte, 2.5 N: Dissolve 33.3 g of NH_4Cl in 150 ml of demineralized water, add 42.2 ml of conc. NH_4OH, and dilute to 250 ml.

5.6 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Stability of hexavalent chromium is not completely understood at this time. Therefore, the analysis should be carried out as soon as possible.

6.3 If the analysis cannot be performed within 24 hr, take an aliquot of the sample and add a known amount of hexavalent chromium (0.1 mg/l for natural waters, 1 mg/l for wastewaters, and 5 mg/l for EP extracts). Analyze this known addition sample at the same time the sample is analyzed to determine whether hexavalent chromium was reduced during storage.

6.4 To retard the chemical activity of hexavalent chromium, the sample should be transported and stored at 4° C until time of analysis.

7.0 Procedure

7.1 Soak the voltammetric cells overnight in 1+1 HNO_3 and/or 1+1 aqua regia.

7.2 Rinse the electrode assembly with demineralized water followed by a rinse with 1 N HNO_3, and finally with demineralized water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 Mode: differential pulse.

7.3.2 Scan rate: 2 mV/sec.

7.3.3 Drop time: 1 sec.

7.3.4 Initial potential: -0.05 V ± 0.05 V vs. Ag/AgCl.

7.3.5 Final potential: -0.50 V ± 0.10 V vs. Ag/AgCl.

7.3.6 Pulse height: 0.05 V.

7.3.7 Deaeration time: 240 sec or less initially, 30 sec between standard additions.

7.4 Analysis

7.4.1 Pipet a volume of sample containing less than 10 µg hexavalent chromium (maximum volume dependent on the voltammetric cell volume, which is usually 10 ml) into a voltammetric cell.

7.4.2 Add 0.5 ml of the ammoniacal electrolyte and adjust volume to 10 ml with demineralized water.

7.4.3 Place the electrode assembly in the solution and outgas with nitrogen for at least 120 sec.

7.4.4 Engage the electrode assembly to the polarographic analyzer and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram.

7.4.5 Figure 2 gives typical differential pulse polarograms.

7.5 Prior to the analysis of any samples, and during analysis at a frequency of at least once every 10 samples, verify that the cell contamination is less than 10 µg/l Cr by analyzing demineralized water and the appropriate volume of supporting electrolyte in a manner similar to the procedure described in 7.4.3 and 7.4.4.

7.6 Calibration

7.6.1 After running a differential pulse polarogram on the sample solution, quantitate the chromium using the technique of standard addition.

7.6.2 Three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration of the sample, the second equal to that of the sample, and the third about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%.

7.6.3 Add an appropriate aliquot of chromium standard solution I, II, or III to the sample in the cell. Deaerate for 30 sec to mix the solution and remove oxygen added with the known addition.

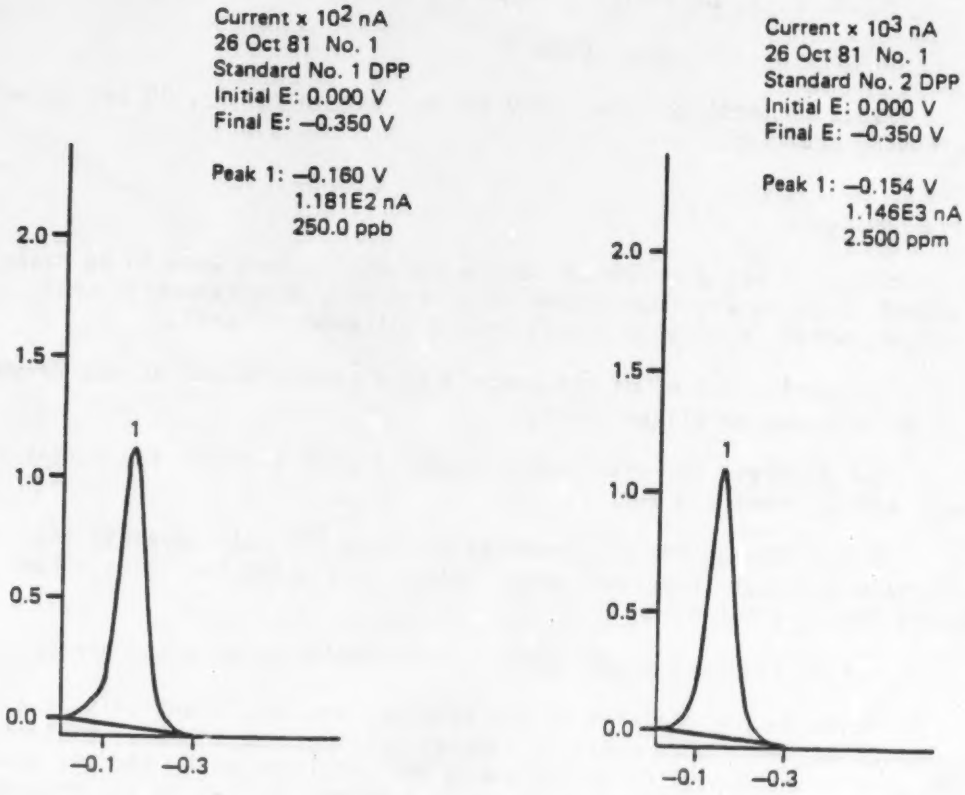


Figure 2. Typical differential pulse polarogram at 0.25 ppm and 2.5 ppm Cr in 0.1 N buffer.

7.6.4 Repeat the analysis procedure beginning with 7.4.4 for each standard addition.

7.7 Calculations

7.7.1 Calculate the concentration of chromium determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 g_i C_s}{i_1 g_i + (i_i - i_1)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA)

i_i = Current peak height for the sample plus standard (nA)

V_u = Volume of sample in the cell (ml)

g_i = Volume of standard taken for spiking (ml)

V = Volume in cell prior to standard addition

C_s = Concentration of standard used to spike (mg/l)

C_u = Concentration of the unknown in the sample (mg/l).

7.7.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 If necessary, dilute samples so they fall within the working range.

8.3 Quantitation must be performed by the method of standard addition.

8.4 Analyze check standards at a rate of approximately one every 15 samples.

8.5 Standards should be compared to a reference standard on a routine basis.

8.6 Precision and accuracy data for this method are summarized in Table 2.

TABLE 2. PRECISION AND ACCURACY OF THE DPP OF HEXAVALENT CHROMIUM

2a. Precision

Sample type	No. of replicates	Average value	% RSD
Leachate[a]	3	1.87	0.69

2b. Accuracy (spike recovery data)

Sample type	Spike level (mg/l)	No. of samples	Average % recovery	Standard deviation of % recovery
EP extracts	5.0	8	92.8	6.4

2c. Methods comparison

	Diff. pulse polarography	APDC extraction ICAP-OES	Ion chromatography coupled to ICAP-OES
Value[a]	1.87	1.84	1.91

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[a] Leachate sample from a waste disposal site.

METHOD 7210

COPPER (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7210 is an atomic absorption procedure approved for determining the concentration of copper in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7210, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the copper concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.02 mg/l; typical sensitivity is 0.1 mg/l for 1% absorption.

3.0 Interferences

3.1 Background correction may be required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Copper hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Copper standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. T. Baker, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.0 g of electrolyte copper (analytical reagent grade) in 5 ml or redistilled HNO_3 and dilute to 1 liter with Type II water.

5.4 Copper working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 324.7-nm wavelength line and background correction shall be used.

7.3 An oxidizing air/acetylene flame shall be employed.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of copper standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7211

COPPER (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7211 is an atomic absorption procedure approved for determining the concentration of copper in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7211, samples must be prepared in order to convert organic forms of copper to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the copper concentration.

2.3 The typical detection limit for this method is 1 μg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, copper analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction may be required to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Copper hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Copper standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. T. Baker, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 100 g of electrolyte copper (analytical reagent grade) in 5 ml redistilled HNO_3 and dilute to 1 liter with Type II water.

5.4 Copper working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 324.7-nm wavelength line shall be used.

7.3 Background correction should be employed.

7.4 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.5 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.6 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.7 Either (1) run a series of copper standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7380

IRON (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7380 is an atomic absorption procedure approved for determining the concentration of iron in wastes, mobility procedure extracts, and soils. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7380, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the iron concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.03 mg/l; typical sensitivity is 0.12 mg/l.

3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Iron hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Iron standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.000 g of iron wire, (analytical reagent grade), and dissolve in Type II water, acidify with 10 ml redistilled HNO_3, and dilute to 1 liter with Type II water.

5.4 Iron working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 248.3-nm wavelength line and background correction shall be used.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of iron standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7381

IRON (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7381 is an atomic absorption procedure approved for determining the concentration of iron in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7381, samples must be prepared in order to convert organic forms of iron to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the iron concentration.

2.3 The typical detection limit for this method is 1 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Iron hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lanthanum nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml concentrated HNO_3 and dilute to 1000 ml with Type II water.

5.4 Iron standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.000 g iron wire (analytical reagent grade) in Type II water and acidify with 10 ml redistilled HNO_3. Dilute to 1 liter.

5.5 Iron working standards: These standards should be prepared such that they contain 0.5% (v/v) HNO_3.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 248.3-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be dilated in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of iron standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7460

MANGANESE (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7460 is an atomic absorption procedure approved for determining the concentration of manganese in wastes, mobility procedure extracts, and soils. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7460, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the manganese concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/l; typical sensitivity is 0.05 mg/l.

3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Manganese hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Manganese standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.000 g of manganese metal (analytical reagent grade) and dissolve in Type II water, acidify with 10 ml redistilled HNO_3, and dilute to 1 liter with Type II water.

5.4 Manganese working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 279.5-nm wavelength line and background correction shall be used.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of manganese standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7461

MANGANESE (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7461 is an atomic absorption procedure approved for determining the concentration of manganese in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7461, samples must be prepared in order to convert organic forms of manganese to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the manganese concentration.

2.3 The typical detection limit for this method is 0.2 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Manganese hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lanthanum nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml concentrated HNO_3 and dilute to 1000 ml with Type II water.

5.4 Manganese standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.000 g of manganese (analytical reagent grade) in Type II water and acidify with 10 ml redistilled HNO_3. Dilute to 1 liter.

5.5 Manganese working standards: These standards should be prepared such that they contain 0.5% (v/v) HNO_3.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 279.5-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be dilated in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of manganese standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7550

OSMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7550 is an atomic absorption procedure approved for determining the concentration of osmium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7550, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure discussed in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable. Due to the very volatile nature of some osmium compounds, the applicability of a method to a sample must be verified by means of spiked samples or standard reference materials or both.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into a nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the osmium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.3 mg/l; typical sensitivity is 1 mg/l or 1% absorption.

3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Due to the volatility of osmium, standards must be made on a daily basis and the applicability of sample preparation techniques must be verified for the sample matrices of interest.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.4 Osmium and its compounds are extremely toxic, so extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Osmium hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Osmium standard stock solution (1000 mg/l): Procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. T. Baker, or Fisher Scientific) and verify by comparison with a second standard. If necessary, standards can be made from osmium compounds. However, due to the toxicity of these compounds, this approach is not advised.

5.4 Osmium working standards: Prepare dilution of the stock solution at the time of analysis. These standards should be prepared to contain 1% (v/v) HNO_3 and 1% (v/v) H_2SO_4.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

5.7 Cylinder of nitrous oxide suitable for instrumental analysis.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to the procedure described in Section 7.2. Sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Sample preparation of aqueous samples

7.2.1 Transfer a representative 100-ml aliquot of the well-mixed sample to a Griffin beaker and add 1 ml of conc. HNO_3.

7.2.2 Place the beaker on a steam bath or hot plate and warm for 15 min. Cool the beaker and, if necessary, filter or centrifuge to remove insoluble material.

7.2.3 Add 1 ml of conc. H_2SO_4 and adjust the volume back to 100 ml. The sample is now ready for analysis.

7.3 The 290.9-nm wavelength line and background correction shall be employed.

7.4 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.5 Follow the manufacturer's operating instructions for all other instrument parameters.

7.6 Either (1) run a series of osmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.9 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7551

OSMIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7551 is an atomic absorption procedure approved for determining the concentration of osmium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7551, samples must be prepared in order to convert organic forms of osmium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable. It is essential that the applicability of the sample preparation technique be verified by means of spiked samples or standard reference materials, or both.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the osmium concentration.

2.3 The typical detection limit for this method is 20 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, osmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Due to the volatility of osmium, standards must be made on a daily basis and the applicability of sample preparative techniques must be verified.

3.5 Osmium and its compounds are extremely toxic, so extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Osmium hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Osmium standard stock solution (1000 mg/l): Procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. T. Baker, or Fisher Scientific), and verify by comparison with a second standard. If necessary, standards can be made from osmium compounds. However, due to the toxicity of these compounds, this approach is not advised.

5.4 Osmium working standards: These standards should be prepared at the time of analysis and they should contain 1% (v/v) HNO_3.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Sample preparation of aqueous samples

7.2.1 Transfer a representative 100-ml aliquot of the well-mixed sample to a Griffin beaker and add 1 ml of conc. HNO_3.

7.2.2 Place the beaker on a steam bath or hot plate and warm for 15 min. Cool the beaker and, if necessary, filter or centrifuge insoluble materials.

7.2.3 Add 1 ml of conc. HNO_3 and adjust volume back to 100 ml.

7.3 The 290.9-nm wavelength line and background correction shall be used.

7.4 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.5 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.6 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.7 Either (1) run a series of osmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7770

SODIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7770 is an atomic absorption procedure approved for determining the concentration of sodium in wastes, mobility procedure extracts, and soils. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7770, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the sodium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.002 mg/l; typical sensitivity is 0.015 mg/l.

3.0 Interferences

3.1 Ionization interferences can affect analysis for sodium, thus samples and standards must be matrix matched or an ionization supressant employed.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Sodium hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Sodium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.542 g of sodium chloride (NaCl), (analytical reagent grade), and dissolve in Type II water, acidify with 10 ml redistilled HNO_3, and dilute to 1 liter with Type II water.

5.4 Sodium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials. All samples and standards must be matrix matched or an ionization suppressant (potassium at 1000 mg/l) must be employed.

7.2 The 589.6-nm wavelength line shall be used.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of sodium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7840

THALLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7840 is an atomic absorption procedure approved for determining the concentration of thallium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7840, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the thallium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/l; typical sensitivity is 0.5 mg/l for 1% absorption.

3.0 Interferences

3.1 Background correction may be required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 The analysis of thallium by atomic absorption spectroscopy has not been investigated with the scrutiny that has been applied to the analysis of other metals. Therefore, caution must be employed to ensure that the analyst does not unknowingly encounter an unreported interference.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate. May elements and anions have been found to enhance the Tl signal and a preliminary separation may be needed.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Thallium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Thallium standard stock solution (1000 mg/l). Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha products, J. T. Baker, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.303 g of thallium nitrate ($TlNO_3$), analytical reagent grade, in Type II water. Add 10 ml of concentrated nitric acid and dilute to 1 liter with Type II water. This compound may be hydrated. Thallium oxide (Tl_2O_3) should be used in lieu of thallium nitrate if hydration of thallium nitrate is suspected.

5.4 Thallium working standards: These standards should be prepared with nitric acid and at the same concentration as the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Section 7.2; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc. HNO_3. Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc. HNO_3. Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2.1 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3, and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with distilled water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 The 276.8-nm wavelength line and background correction shall be employed.

7.4 An oxidizing air/acetylene flame shall be used.

7.5 Follow the manufacturer's operating instructions for all other instrument parameters.

7.6 Either (1) run a series of thallium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.9 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7841

THALLIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7841 is an atomic absorption procedure approved for determining the concentration of thallium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7841, samples must be prepared in order to convert organic forms of thallium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the thallium concentration.

2.3 The typical detection limit for this method is 1 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, thallium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Thallium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Thallium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J.T. Baker, or Fisher Scientific), and verify by comparison with a second standard, or dissolve 1.303 g of thallium nitrate ($TlNO_3$), analytical reagent grade, in Type II water. Add 10 ml of conc. HNO_3 and dilute to 1 liter with Type II water. This compound may be hydrated. Thallium oxide (Tl_2O_3) should be used in lieu of thallium nitrate if hydration of thallium is suspected.

5.4 Thallium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 276.8-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of thallium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7910

VANADIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7910 is an atomic absorption procedure approved for determining the concentration of vanadium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7910, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the vanadium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.2 mg/l; typical sensitivity is 0.8 mg/l for 1% absorption.

3.0 Interferences

3.1 Background correction may be required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 High concentrations of aluminum or titanium as well as Bi, Cr, Co, Fe, K, Li, Na, Acetic Acid, Phosphoric Acid, and detergents may increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Vanadium hollow cathode lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Aluminum nitrate solution: Dissolve 139 g aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$, in 150 ml of Type II water; heat to complete dissolution. Allow to cool and dilute to 200 ml.

5.4 Vanadium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, J. T. Baker, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.7854 g of vanadium pentoxide (V_2O_5), analytical reagent grade, in 10 ml of concentrated nitric acid and dilute to 1 liter with Type II water.

5.5 Vanadium working standards: These standards should be prepared at the time of analysis with the same type of acid and at the same concentration as the analytical solution. If an aluminum or titanium interference is expected, add 2 ml of the aluminum nitrate solution to 100 ml of each standard and sample. Matrix matching of standards to samples may be necessary, if the matrix contains other elements (Refer to 3.2).

5.6 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.7 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

5.8 Nitrous oxide cylinder: Suitable for instrumental analysis.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 318.4-nm wavelength line and background correction shall be employed.

7.3 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.5 Either (1) run a series of vanadium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7911

VANADIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7911 is an atomic absorption procedure approved for determining the concentration of vanadium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7911, samples must be prepared in order to convert organic forms of vanadium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the vanadium concentration.

2.3 The typical detection limit for this method is 4 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, vanadium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures. Memory effects are not uncommon in vanadium analysis since vanadium is refractory and also has a tendency to form carbides.

3.4 Nitrogen is not recommended as a purge gas because of possible chemical interaction.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Vanadium hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Vanadium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha products, J. T. Baker, or Fisher Scientific), and verify by comparison with a second standard, or dissolve 1.7854 g of vanadium pentoxide (V_2O_5), analytical reagent grade, in 10 ml of concentrated nitric acid and dilute to 1 liter with Type II water.

5.4 Vanadium working standards: These standards should be prepared to contain 0.5% (v/v) HNO_3.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 318.4-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of vanadium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7950

ZINC (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

1.0 Scope and Application

1.1 Method 7950 is an atomic absorption procedure approved for determining the concentration of vanadium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7950, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the zinc concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.005 mg/l; typical sensitivity is 0.05 mg/l for 1% absorption.

3.0 Interferences

3.1 Background correction may be required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Since zinc is a universal contaminant, great care must be taken to ensure that samples and standards are not contaminated.

3.3 High levels of silicon as well as copper and phosphate at concentrations greater than 100 μg/ml. Addition of strontium (1500 μg/ml) remove the copper and phosphate interference.

3.4 Perchloric and sulfuric acids will cause slight depressions in the absorption signal. Acid matching the sample and standards will solve this problem.

3.5 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Zinc hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Zinc standard stock solution (1000 mg/l). Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1 g of zinc metal (analytical reagent grade) in 10 ml HNO_3 and dilute to 1 liter with Type II water.

5.4 Zinc working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 213.9-nm wavelength line and background correction shall be employed.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of zinc standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 μg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7951

ZINC (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7951 is an atomic absorption procedure approved for determining the concentration of vanadium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7951, samples must be prepared in order to convert organic forms of zinc to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the zinc concentration.

2.3 The typical detection limit for this method is 0.05 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, zinc analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Most elements interfere with zinc analysis when they are present in large amounts. Solvent extraction procedures avoid these problems.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Zinc hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Zinc standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1 g of zinc metal (analytical reagent grade) in 10 ml HNO_3 and dilute to 1 liter with Type II water.

5.4 Zinc working standard: These standards should be prepared at the time of analysis and should contain 0.5% (v/v) HNO_3.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 213.9-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of zinc standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 8320

MISCELLANEOUS COMPOUNDS

1.0 Scope and Application

Method 8320 may be used to determine the concentration of certain compounds using HPLC. Specifically, Method 8320 is used to detect the following compounds:

3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts (Warfarin)
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-methoxy-5-methylcarbamate azirino(2',3':3,4)pyrrolo(1,1a-)indole-4,7-dione(ester) (Mitomycin C)
Chlorambucil
Daunomycin
Melphalan
Methomyl
5-Nitro-o-toluidine
Reserpine
Streptozotocin
Thiuram

1.2 Method 8320 is applicable to a variety of matrices including organic liquids, organic solids, sludges, aqueous liquids, and groundwater.

1.3 Use of Method 8320 presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2.0 Summary of Method

2.1 One-liter aqueous samples are extracted using either methods 3510 or 3530. Organic liquids may be analyzed neat or diluted with an appropriate solvent. Solid samples are extracted using either method 3540 or 3550. Extracts are concentrated to 10 ml before analysis.

2.2 Table 1 lists the appropriate solvents used for each compound and corresponding LC conditions.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All these materials must be demonstrated to be

TABLE 1. HPLC AND EXTRACTION PARAMETERS

Compound	Solvent	Extraction pH	HPLC conditions[a]
Warfarin	Diethyl ether	7	A
Mitomycin C	Diethyl ether	7	A
Chlorambucil	Diethyl ether	7	A
Daunomycin	Diethyl ether	7	B
Melphalan	Diethyl ether	7	A
Methomyl	Diethyl ether	7	A
5-Nitro-o-toluidine	Diethyl ether	7	A
Reserpine	Diethyl ether	7	A
Streptozotocin	Diethyl ether	7	A
Thiuram	Diethyl ether	7	A

[a] HPLC conditions:

A	Column:	Perkin Elmer HC ODS Sil-X or equivalent. Reverse phase column, 10 μm particle size, 25 cm x 2.6 mm I.D.
	Temperature:	30° C
	Solvents:	A - Distilled water B - Acetonitrile
	Flow Rate:	1 ml/min
	Program:	10% B, 5 min; 10 to 100% B in 35 min; 100% B, 10 min.
B	Column:	Same as A
	Temperature:	Same as A
	Solvents:	A - 1% (v/v) HOAc in distilled water B - Acetonitrile
	Flow Rate:	2 ml/min
	Program:	20% B, 10 min; 20 to 50% B in 10 min; 50% B, 5 min.

free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the chromatographic conditions described allow for a unique resolution of the specific compounds covered by this method, other compounds may interfere.

4.0 Apparatus and Materials

4.1 HPLC apparatus

4.1.1 Gradient pump system, constant flow.

4.1.2 Reverse phase column, 10 µm HC-ODS Sil-X, 25 cm x 2.6 mm I.D.

4.1.3 UV detector, 254 nm.

4.1.4 Strip chart recorder compatible with detector or data acquisition system.

5.0 Reagents

5.1 Deionized distilled water.

5.2 Glacial acetic acid made up to 1% (v/v) with deionized distilled water.

5.3 Diethyl ether, high purity.

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g of assayed reference material in ether, ethyl acetate, or other appropriate solvent and diluting to volume in a 100-ml ground-glass-stoppered volumetric flask. The stock solution is transferred to ground-glass-stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Acetonitrile: Spectral quality.

5.6 Ethyl acetate: Spectral quality.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

6.3 The samples must be iced or refrigerated from the time of collection until extraction.

6.4 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

7.0 Procedure

7.1 Calibration

7.1.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will completely bracket the working range of the chromatographic system.

7.1.2 Assemble the necessary HPLC apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

7.1.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.2 High Performance Liquid Chromatography (HPLC)

7.2.1 Table 1 summarizes the recommended HPLC column materials and operating conditions for the instrument. Calibrate the system daily with a minimum of three injections of calibration standards.

7.2.2 Inject 2-5 µl of the sample extract with a high pressure syringe or sample injection loop. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.2.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.2.4 If the peak area measurement is prevented by the pressure of interference, further cleanup is required.

7.3 Calculations

7.3.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

where:

A = Calibration factor for chromatographic system (in ng material per area unit)

B = Peak size in injection of sample extract (in area units)

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml).

7.3.2 Report results in µg/l without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate, through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified waste samples should be analyzed to validate the accuracy of the analysis.

METHOD 8330

THIOUREAS AND OTHER COMPOUNDS

1.0 Scope and Application

Method 8330 may be used to determine the concentration of certain thioureas and other compounds. Specifically, Method 8330 is used to detect the following compounds:

Azaserine
N-Nitroso-N-methylurea
1-Acetyl-2-thiourea
1-(o-Chlorophenyl)thiourea
Citris Red N
Crotonaldehyde
Diethylstilbestrol (DES)
3,4-Dihydroxy-alpha-(methylamine)methyl benzyl alcohol (Epinephrine)
Ethylenethiourea
1-Naphthyl-2-thiourea
N-Phenylthiourea
Thioacetamide
Thiosemicarbazide
Thiourea
Trypan blue

1.2 Method 8330 is applicable to a variety of matrices including organic liquids, organic solids, sludges, aqueous liquids, and groundwater.

1.3 Use of Method 8330 presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2.0 Summary of Method

2.1 One-liter aqueous samples are extracted using either methods 3510 or 3530. Organic liquids may be analyzed neat or diluted with an appropriate solvent. Solid samples are extracted using either method 3540 or 3550. Extracts are concentrated to 10 ml before analysis.

2.2 Table 1 lists the appropriate solvents used for each compound and corresponding LC conditions.

TABLE 1. HPLC AND EXTRACTION PARAMETERS

Compound	Solvent	Extraction pH	HPLC conditions[a]
Azaserine	Diethyl ether	7	A
N-Nitroso-N-methyl urea	Diethyl ether	7	A
1-Acetyl-2-thiourea	Diethyl ether	7	B
1-(o-Chlorophenyl)thiourea	Diethyl ether	7	B
Citris Red N	Diethyl ether	7	B
Crotonaldehyde	Diethyl ether	7	B
DES	Diethyl ether	7	B
Epinephrine	Diethyl ether	7	B
Ethylenethiourea	Diethyl ether	7	B
1-Naphthyl-2-thiourea	Diethyl ether	7	B
N-Phenylthiourea	Diethyl ether	7	B
Thioacetamide	Diethyl ether	7	B
Thiosemicarbazide	Diethyl ether	7	B
Thiourea	Diethyl ether	7	B
Trypan blue	Diethyl ether	7	B

[a] HPLC conditions:

A	Column:	µ Bondpak C_{18} or equivalent. Reverse phase column, 10 µm particle size, 30 cm x 3.9 mm I.D.
	Temperature:	30° C
	Solvents:	A - Distilled deionized water B - Acetonitrile
	Flow Rate:	1 ml/min
	Program:	2% B, isocratic
B	Column:	Same as A
	Temperature:	Same as A
	Solvents:	Same as A
	Flow Rate:	Same as A
	Program:	20% B to 100% B in 20 min; 100% B for 10 min.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the chromatographic conditions described allow for a unique resolution of the specific compounds covered by this method, other compounds may interfere.

4.0 Apparatus and Materials

4.1 HPLC apparatus

4.1.1 Gradient pump system, constant flow

4.1.2 Column: Waters Associates µ Bondpak C_{18} or equivalent. Reverse phase column, 10 µm particle size, 30 cm x 3.9 mm I.D.

4.1.3 UV detector, 254 nm.

4.1.4 Strip chart recorder compatible with detector or data acquisition system.

5.0 Reagents

5.1 Deionized distilled water.

5.3 Diethyl ether, high purity.

5.3 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g of assayed reference material in ether, ethyl acetate, or other appropriate solvent and diluting to volume in a 100-ml ground-glass-stoppered volumetric flask. The stock solution is transferred to ground-glass-stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.4 Acetonitrile: Spectral quality.

5.5 Ethyl acetate: Spectral quality.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

6.3 The samples must be iced or refrigerated from the time of collection until extraction.

6.4 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

7.0 Procedure

7.1 Calibration

7.1.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will completely bracket the working range of the chromatographic system.

7.1.2 Assemble the necessary HPLC apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

7.1.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.2 High Performance Liquid Chromatography (HPLC)

7.2.1 Table 1 summarizes the recommended HPLC column materials and operating conditions for the instrument. Calibrate the system daily with a minimum of three injections of calibration standards.

7.2.2 Inject 2-5 µl of the sample extract with a high pressure syringe or sample injection loop. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.2.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.2.4 If the peak area measurement is prevented by the pressure of interference, further cleanup is required.

7.3 Calculations

7.3.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

where:

A = Calibration factor for chromatographic system (in ng material per area unit)

B = Peak size in injection of sample extract (in area units)

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml).

7.3.2 Report results in μg/l without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate, through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified waste samples should be analyzed to validate the accuracy of the analysis.

METHOD 8410

FORMALDEHYDE: BASIC MEDIUM

1.0 Scope and Application

1.1 Method 8410 is a differential-pulse polarographic method which is used for determining the concentration of formaldehyde in groundwaters, EP extracts, and wastes.

1.2 This method is applicable to concentrations ranging from 0.5 ppm to 100 ppm.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of polarography, the interpretation of polarograms, and the detection of electrochemical interferences.

2.0 Summary of Method

2.1 The sample is diluted with electrolyte and placed in an analytical cell. Since formaldehyde is electroactive at the dropping mercury electrode (DME) and is reduced to methanol, a current is generated. This current is kinetically controlled and is proportional to the concentration of formaldehyde.

3.0 Interferences

3.1 Most polarographic measurements are diffusion controlled. Formaldehyde analysis is kinetically controlled by the dehydration reaction which frees formaldehyde molecules for reduction at the DME. Due to this kinetic factor the analysis is sensitive to changes in pH and temperature. The pH can be controlled by use of a buffer or a high pH electrolyte.

3.2 The reduction of sodium and potassium present in solution can interfere with the determination of formaldehyde. Thus a lithium salt is employed as the electrolyte salt. To eliminate interference from residual sodium and potassium, a buffer of pH 11 is used to shift the formaldehyde peak.

3.3 Formaldehyde, in basic solutions, can undergo a Cannizzaro reaction which yields electroinactive products. The analysis should be performed within 30 min of preparation.

3.4 Concentrations of acetaldehyde greater than 10 times the concentration of formaldehyde prevent the determination of formaldehyde concentrations. Other aldehydes can also cause interferences. It is possible to eliminate these interferences in solution by changing the pH which results in a shift in the formaldehyde peak potential.

4.0 Apparatus and Materials

4.1 A polarographic system capable of operating in a differential-pulse mode with a scan rate of 2-5 mV/sec.

4.2 Dropping mercury electrode (DME) assembly capable of performing differential pulse analyses.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193) should be monitored for impurities.

5.2 Electrolyte solution: 0.1 M lithium hydroxide/0.1 M lithium chloride.

5.3 Formaldehyde standard, 1000 ppm, made from 37% formaldehyde solution standardized according to the U.S. Pharmacopeia method.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Stability of formaldehyde is not completely understood. Therefore analysis should be carried out as soon as possible.

7.0 Procedure

7.1 Prepare the sample by dilution with the electrolyte solution. The dilution factor will be dictated by the concentration of formaldehyde in the sample. The dilution should result in formaldehyde concentrations which fall within the working range of the polarographic system being used.

7.2 Rinse the electrode with deionized water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 Mode: Differential pulse.

7.3.2 Scan rate: 2-5 mV/sec.

7.3.3 Drop time: 1 sec.

7.3.4 Initial potential: -1.3 V vs. Ag/AgCl.

7.3.5 Peak potential: 1.6 ± 0.05 V vs. Ag/AgCl.

7.3.6 Deaeration time: 4 min.

7.4 Place the sample and electrolyte in the cell. Deaerate the sample and begin the analysis immediately.

7.5 Engage the electrode assembly to the polarographic analyzer and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram. (Figure 1 gives a typical polarogram for formaldehyde solution analyzed in this manner.)

7.6 After a differential pulse polarogram is run on the sample solution, the formaldehyde concentration will be determined by the method of standard additions. A total of three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration found in the sample, the second should be equal to that of the sample, and the third should be about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%. Standards should be spiked directly into the cell.

7.7 Repeat the analysis procedure beginning with step 7.4 for each standard addition.

7.8 Calculations

7.8.1 Calculate the concentration of formaldehyde determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 \gamma_i C_s}{i_1 \gamma_i + (i_i - i_1)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA)

i_i = Current peak height for the sample plus standard (nA)

V_u = Volume of sample in the cell (ml)

γ_i = Volume of standard taken for spiking (ml)

V = Volume in cell prior to standard addition

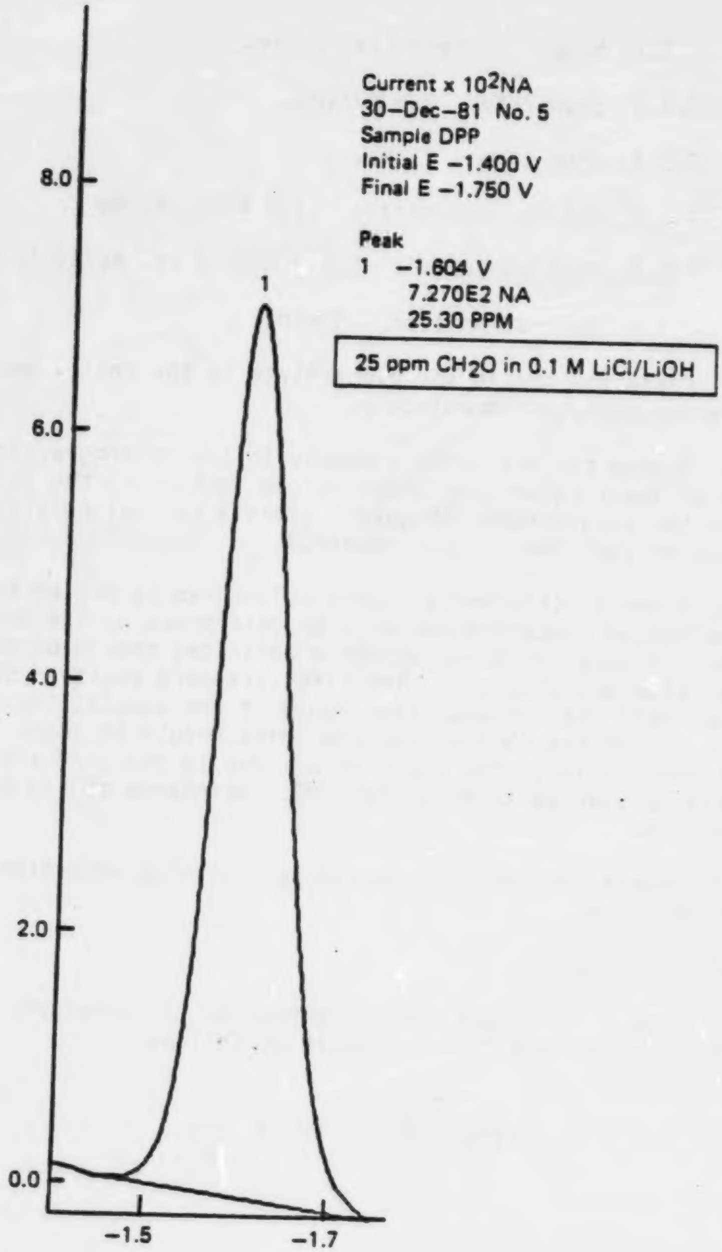

Figure 1. Polarogram of formaldehyde solution (basic medium).

C_s = Concentration of standard used to spike (mg/l)

C_u = Concentration of the unknown in the sample (mg/l).

7.8.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Quantitation must be performed by the method of standard addition.

8.3 Analyze check standards at a rate of approximately one every 15 samples.

METHOD 8411

FORMALDEHYDE: ACIDIC MEDIUM

1.0 Scope and Application

1.1 Method 8411 is a differential-pulse polarographic method which is used for determining the concentration of formaldehyde in groundwaters, EP extracts, and wastes.

1.2 This method is applicable to concentrations ranging from 25 ppb to 2000 ppb.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of polarography, the interpretation of polarograms, and the detection of electrochemical interferences.

2.0 Summary of Method

2.1 Since the direct reduction of formaldehyde in acid media is not feasible, the sample is treated to form a hydrazone derivative of formaldehyde. The hydrazone derivative is then reduced at the dropping mercury electrode (DME). The peak height is proportional to formaldehyde concentration.

3.0 Interferences

3.1 Samples and electrolyte solutions will often contain materials that will react with the hydrazone reagent. An excess of hydrazone is added to ensure that enough reagent remains to react with the formaldehyde.

3.2 The preparation of a clean blank is very difficult. To ensure an acceptable blank, the electrolyte solution must be made daily. Freshly prepared blanks can have a peak height at -0.9 volts of as much as 40 nA. This blank level must be subtracted from the sample peak height.

3.3 Concentrations of acetaldehyde greater than 10 times the concentration of formaldehyde prevent the determination of formaldehyde concentrations. Other aldehydes can also cause interferences. It may be possible to eliminate these interferences by separating the aldehydes by a technique such as liquid chromatography.

4.0 Apparatus and Materials

4.1 A polarographic system capable of operating in a differential-pulse mode with a scan rate of 2-5 mV/sec.

4.2 Dropping mercury electrode (DME) assembly capable of performing differential pulse analyses.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193) should be monitored for impurities.

5.2 Electrolyte solution: 0.1 M acetate buffer at pH 4.5 containing 0.2% hydrazine hydrochloride. To obtain the lowest blank the electrolyte should be prepared in the cell by adding the acetate buffer, the hydrazine, and the sample as separate aliquots. Thus the acetate buffer should be prepared at a concentration of 2.5 M and the hydrazine hydrochloride at a concentration of 2.0%.

5.3 Formaldehyde standard, 1000 ppm, made from 37% formaldehyde solution standardized according to the U.S. Pharmacopeia method.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Stability of formaldehyde is not completely understood. Therefore analysis should be carried out as soon as possible.

7.0 Procedure

7.1 To an appropriate sample volume add 4.0 ml of the 2.5 M acetate buffer and 1 ml of the 2% hydrazine hydrochloride solution. The sample volume should be chosen to give a formaldehyde concentration within the working range. The reaction of hydrazine with the formaldehyde is not immediate. The sample and the electrolyte solution should be mixed and allowed to stand for at least 5 min (but no more than 1 hr) before running the polarogram.

7.2 Rinse the electrode with deionized water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 Mode: Differential pulse

7.3.2 Scan rate: 2-5 mV/sec

7.3.3 Drop time: 1 sec.

7.3.4 Initial potential: -0.7 V vs. Ag/AgCl.

7.3.5 Peak potential: 0.9 ± 0.05 V vs. Ag/AgCl.

7.3.6 Deaeration time: 4 min.

7.4 Place the sample and electrolyte in the cell, mix, and let stand for at least 5 min. Deaerate and begin analysis immediately.

7.5 Engage the electrode assembly to the potentiostat and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram. (Figure 1 gives a typical polarogram for formaldehyde solution analyzed in this manner.)

7.6 After a differential pulse polarogram is run on the sample solution, the formaldehyde concentration will be determined by the method of standard additions. A total of three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration found in the sample, the second should be equal to that of the sample, and the third should be about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%. Standards should be spiked directly into the cell.

7.7 Repeat the analysis procedure beginning with step 7.4 for each standard addition.

7.8 Calculations

7.8.1 Calculate the concentration of formaldehyde determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 \gamma_i C_s}{i_1 \gamma_i + (i_i - i_1)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA)
i_i = Current peak height for the sample plus standard (nA)
V_u = Volume of sample in the cell (ml)
γ_i = Volume of standard taken for spiking (ml)
V = Volume in cell prior to standard addition
C_s = Concentration of standard used to spike (mg/l)
C_u = Concentration of the unknown in the sample (mg/l).

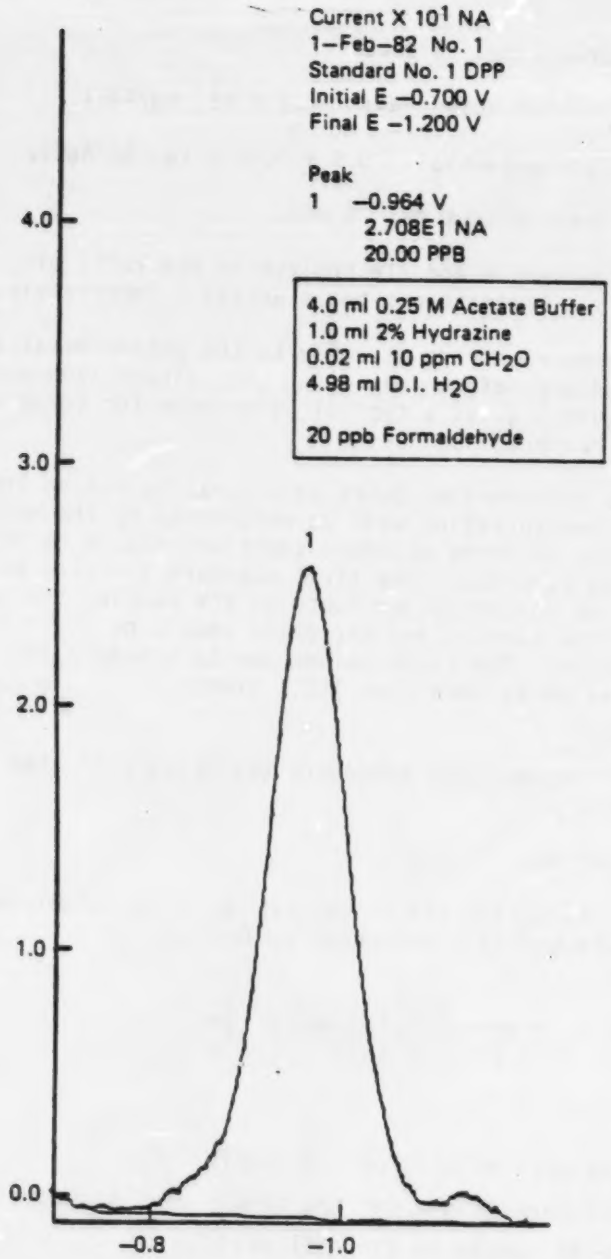

Figure 1. Polarogram of formaldehyde solution (acidic medium).

7.8.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 If necessary, dilute samples so they fall within the working range.

8.3 Quantitation must be performed by the method of standard addition.

8.4 Analyze check standards at a rate of approximately one every 15 samples.

METHOD 8600

HIERARCHICAL ANALYTICAL PROTOCOL FOR GROUNDWATER

1.0 Scope and Application

1.1 Method 8600 is a comprehensive analytical scheme designed for the analysis of Part 261 Appendix VIII compounds in groundwater. Method 8600 may only be used to demonstrate the presence or absence of Appendix VIII compounds in groundwater as required by Parts 264.98 and 264.99 and is not approved for any other use.

1.2 Method 8600 covers the detection and quantification of all of the compounds listed on Appendix VIII with the exception of the following:

Acetyl chloride
Alumimum phosphide
Carbon oxyfluoride
Cycasin
Dimethylcarbamoyl chloride
Ethylenebisdithiocarbamic acid, salts and esters
Fluorine
2-Fluoroacetamide
Hydrofluoric acid
Iron dextran
Isocyanic acid, methyl ester
Lasiocarpine
Methyl chlorocarbonate
Mustard gas
Nitric oxide
Nitrogen dioxide
Nitrogen mustard and HCL salt
Nitrogen mustard N-oxide and HCL salt
Phosgene
Phosphine
Toluene diisocyanate
Zinc phosphide

1.3 This method is recommended for use by, or under the supervision of, analysts experienced in the use of techniques and operation of equipment necessary to perform the screening methods used in the decision matrix.

2.0 Summary of Method

2.1 Method 8600 relies on results obtained from a number of screening methods and arrays these results into a decison matrix. In utilizing this matrix a large number of compounds may be eliminated.

2.2 The overall logic scheme employed in Method 8600 is provided in Figure 1.

2.3 A positive test is indicated by comparing the results obtained by the referenced screening method from the upgradient vs. the downgradient groundwater sample. Each of the 8600 series methods used in the decision matrix provides detailed instructions explaining how a pass/fail or high/low determination is made.

3.0 Interferences

3.1 Interferences are dealt with in each of the 8600 series methods individually.

4.0 Apparatus and Materials

4.1 Apparatus and materials necessary in the use of the methods in the 8600 series are described in the individual methods.

5.0 Reagents

5.1 Reagents used in the 8600 series methods are indicated in each individual method.

6.0 Sample Collection, Preservation, Handling

6.1 All samples must be collected using sampling procedures described in Section 3.1 of this manual.

6.2 Collection, preservation, and handling procedures specified in each of the individual series 8600 methods should be adhered to.

6.3 Samples and extracts should be stored at 4°C until analysis. Sample holding times should not exceed 4 weeks.

7.0 Procedure

7.1 Use of the Method 8600 logic scheme allows the analyst to determine the presence or absence of the compounds in the groundwater sample as they are listed on Tables 1 thru 9. They are listed on these tables based on properties identifiable through the use of the appropriate analytical method.

Figure 1. Method 8600 Decision Matrix

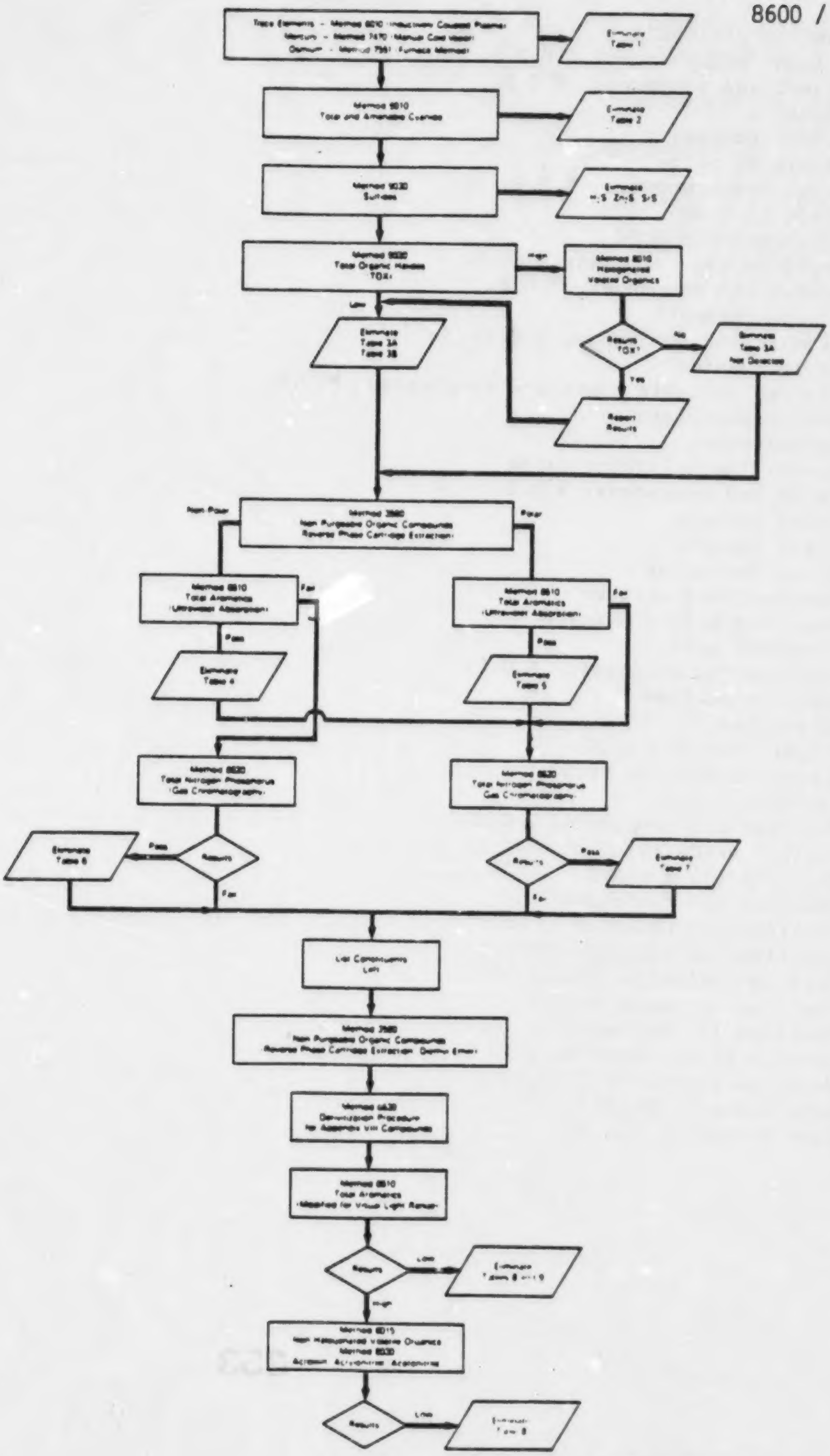
Trace Elements – Method 6010 (Inductively Coupled Plasma)
Mercury – Method 7470 (Manual Cold Vapor)
Osmium – Method 7561 (Furnace Method)
Eliminate Table 1
Method 9010 Total and Amenable Cyanide
Eliminate Table 2
Method 9030 Sulfides
Eliminate HgS ZnS SnS
Method 9020 Total Organic Halides (TOX)
High
Method 8010 Halogenated Volatile Organics
Low
Eliminate Table 3A Table 3B
Results TOX?
No
Eliminate Table 3A Not Detected
Yes
Report Results
Non Polar
Method 3580 Non Purgeable Organic Compounds (Reverse Phase Cartridge Extraction)
Polar
Method 8610 Total Aromatics (Ultraviolet Absorption)
Fail
Pass
Eliminate Table 4
Method 8610 Total Aromatics (Ultraviolet Absorption)
Fail
Pass
Eliminate Table 5
Method 8620 Total Nitrogen Phosphorus (Gas Chromatography)
Method 8620 Total Nitrogen Phosphorus (Gas Chromatography)
Eliminate Table 6
Pass
Results
Fail
Results
Pass
Eliminate Table 7
Fail
List Constituents Left
Method 3580 Non Purgeable Organic Compounds (Reverse Phase Cartridge Extraction: Diethyl Ether)
Method 8630 Derivatization Procedure for Appendix VIII Compounds
Method 8610 Total Aromatics (Modified for Visual Light Range)
Results
Low
Eliminate Tables 8 and 9
High
Method 8015 Non Halogenated Volatile Organics
Method 8030 Acrolein Acrylonitrile Acetonitrile
Results
Low
Eliminate Table 8

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Table 1 TRACE ELEMENTS, MERCURY, AND OSMIUM COMPOUNDS

Aluminum phosphide
Antimony and compounds, N.O.S.
Arsenic and compounds, N.O.S.
Arsenic acid
Arsenic pentoxide
Arsenic trioxide
Barium and compounds, N.O.S.
Barium cyanide
Benzenearsonic acid
Beryllium and compounds, N.O.S.
Cadmium and compounds, N.O.S.
Calcoum chromate
chromium and compounds, N.O.S.
Copper cyanide
Cyanides (soluble salts and complexes), N.O.S.
Dichlorophenylarsine
Diethylarsine
Hydroxydimethylarsine oxide
Nickel and compounds, N.O.S.
Nickel carbonyl
Nickel cyanide
Osmium Tetroxide
Phenylmercury acetate
Potassium silver syanide
Selenious acid
Selenium and compounds, N.O.S.
Selenium sulfide
Selenourea
Silver cyanide (AgCN)
Strontium sulfide (SrSO
Tetraethyl lead
Thallium and compounds, N.O.S.
Thallic oxide (Tl_2O_3)
Thallium (I) acetate
Thallium (I) carbonate
Thallium (I) chloride (TlCl)
Thallium (I) nitrate ($TlNO_3$)
Thallium selenite (TlSe)
Thallium selenite (TlSe)
Thallium (I) sulfate
Vanadic acid, ammonium salt
Vanadium pentoxide (V_2O_5)
Zinc cyanide ($Zn(CN)_2$)
Zinc phosphide (Zn_3P_2)

Table 2 CYANIDE COMPOUNDS

Barium cyanide
Calcium cyanide
Copper cyanide
Cyanogen
Cyanogen bromide
Cyanogen chloride
Hydrocyanic acid
Nickel cyanide
Potassium cyanide
Potassium silver cyanide
Silver cyanide ($AgCN$)
Sodium cyanide ($NaCN$)
Zinc cyanide ($Zn(CN)_2$)

Table 3 VOLATILE HALOGENATED ORGANICS

Bis(2-chloroethoxy)methane
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(chloromethyl) ether
Bromoacetone
Bromomethane
Chloral
Chlorinated benzenes, N.O.S.
Chlorinated ethane, N.O.S.
Chlorinated fluorocarbons, N.O.S.
Chloroalkyl ethers, N.O.S.
Chlorobenzene
1-Chloro-2,3-epoxypropane
2-Chloroethyl vinyl ether
Chloroform
Chloromethane
Chloromethyl methyl ether
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
trans-1,2-Dichloroethene
Dichloroethylene, N.O.S.
1,1-Dichloroethylene
Dichloromethane
Dichloropropane, N.O.S.
1-2-Dichloropropane
Dichloropropene, N.O.S.
1-3-Dichloropropene
Halomethane, N.O.S.
Hexachloroethane
Hexachloropropene
Iodomethane
Tetrachloroethane, N.O.S.
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethane
Tetrachloromethane
Tribromomethane
1,1,1-trichloroethane
1,1,2-trichloroethane
Trichloroethene
Trichloromonofluoromethane
Trichloropropane, N.O.S.
1,2,3-Trichloropropane
Vinyl chloride

Table 3B SEMI-VOLATILE HALOGENATED ORGANICS

Aldrin
Aromite
Benxene, dichloromethyl-
Benzotrichloride
Benxyl chloride
N,N-Bis(2-chloroethyl)-2-naphthylamine
4-Bromophenyl phenyl ether
Chloridane
Chlorinated benzenes, N.O.S.
Chlorinated maphthalene, N.O.S.
Chlorinated phenol, N.O.S.
Chloroacetaldehyde
Chloroalkyl ethers, N.O.S.
Chlorobenzilate
p-Chloro-m-cresol
2-Chlorophenol
3-Chloropropionitrile
Cyclophosphamide
DDD
DDE
DDT
Diallate
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
Dichlorobenzene, N.O.S.
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dichlorophenoxyacetic acid, salts and esters (2,3-D)
Dichloropropanol, N.O.S.
Endosulfan
Endrin and metabolites
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane (all isomers) (Lindane and isomers)
Hexachlorocyclopentadiene
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene
Hexachlorophene
Kepone
Methoxychlor
Methylchlorocarbonate
4,4'-Methylenebis (2-chloroaniline)
Pentachlorobenzene
Pentachloroethane
Pentachloronitrobenzene (PCNB)
Pentachlorophenol
Polychlorinated biphenyls, N.O.S.
Pronamide
1,3-Propane sultone
1,2,4,5-Tetrachlorobenzene

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
2,3,4,6-Tetrachlorophenol
Toxaphene
1,2,4-Trichlorobenxene
Trichloromethanethiol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)
Tris (2-3-dibromopropyl) phosphate

TABLE 5 - UV ACTIVE, SEMI VOLATILE POLAR ORGANICS

Acetophenone
3-(alpha-Acetonylbenzyl)-4-hydroxycourmarin, and salts
2-Acetylaminoflourene
4-Aminobiphenyl
5-(Aminomethyl)-3-isoxazolol
Amitrole
Aniline
Aramite
Auramine
Benzenethiol
Benzidine
p-Benzoquinone
N,N-Bis(2-chloroethyl)-2-naphthylamine
Bis(2-ethylhexyl) phthalate
Brucine
Butyl benzyl phthalate
2-sec-Butyl-2,4-dinitrophenol (DNBP)
Chlorobenzilate
p-Chloro-m-cresol
2-Chlorophenol
Coal tars
Creosote
2-Cyclohexyl-4,6-dinitrophenol
Diallate
Di-n-butyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dichlorophenoxyacetic acid, salts and esters (2,4-D)
0,0-Diethylphosphoric acid, 0-p-nitrophenyl ester
Diethyl phthalate
Diethylstilbesterol
Dihydrosafrole
3,3'-Dimethoxybenzidine
p-Dimethylaminoazobenzene
3,3'-Dimethylbenzidine
alpha,alpha-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethyl phthalate
Dinitrobenzene, N.O.S.
4,6-Dinitro-o-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
Diphenylamine
1,2-Diphenylhydrazine
Isosafrole

TABLE 5 - (Continued)

Maleic hydrazide
Methapyrilene
4,4'-Methylenebis(2-chloroaniline)
Methyl parathion
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
Nicotine and salts
p-Nitroaniline
Nitrobenzine
4-Nitrophenol
Parathion
Pentachloronitrobenzene (PCNB)
Pentachlorophenol
Phenacetin
Phenylenediamine
Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)-sulfonyl)phenyl) ester
Phthalic acid esters, N.O.S.
Phthalic anhydride
2-Picoline
Propylthiouracil
Pyridine
Resorcinol
Safrole
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)

TABLE 6 - N/P CONTAINING, UV ACTIVE NON-POLAR ORGANICS

Dibenz(a,h)acridine
Dibenz(a,j)acridine
7H-Dibenzo(c,g)carbazole

TABLE 7 - N/P CONTAINING, UV ACTIVE POLAR ORGANICS

1-Acetyl-2-thiourea
4-Aminobiphenyl
5-(Aminomethyl)-3-isoxazolol
Amitrole
Aniline
Auramine
Benzidine
N,N-Bis(2-chloroethyl)-2-naphthylamine
Brucine
2-sec-Butyl-2,4-dinitrophenol (DNBP)
3-Chloropropionitrile
2-Cyclohexyl-4,6-dinitrophenol
Cyclophosphamide
Diallate
3,3'-Dichlorobenzidine
N,N-Diethylhydrazine
O,O-Diethyl O-2-pyrazinyl phosphorothioate
Dimethoate
3,3'-Dimethoxybenzidine
p-Dimethylaminoazobenzene
3,3'-Dimethylbenzidine
1,1-Dimethylhydrazine
1,2-Dimethylhydrazine
3,3-Dimethyl-1-(methylthio)-2-butanone
alpha,alpha-Dimethylphenethylamine
Dinitrobenzene, N.O.S.
4,6-Dinitro-o-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Diphenylamine
1,2-Diphenylhydrazine
Di-n-propylnitrosamine
2,4-Dithiobiuret
Ethyl carbamate
Ethyl cyanide
Ethyleneimine
Ethylenethiourea
Hydrazine
Maleic hydrazide
Malononitrile
Methapyrilene
Metholmyl
2-Methylaziridine
4,4'-Methylenebis(2-chloroaniline)
2-Methyllactonitrile
2-Methyl-2-(methylthio)propionaldehyde-o-(methylcarbonyl) oxime
N-Methyl-N'-nitro-N-Nitrosoguanidine
Methyl parathion
Methylthiouracil

TABLE 7 - (Continued)

1-Napthylamine
2-Napthylamine
1-Naphthyl-2-thiourea
Nicotine and salts
p-Nitroaniline
Nitrobenzine
Nitroglycerin
4-Nitrophenol
4-Nitroquinoline-1-oxide
Nitrosamine, N.O.S.
N-Nitrosodi-n-butylamine
N-Nitrosodiethanolamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
N-Nitroso-N-ethylurea
N-Nitrosomethylethylamine
N-Nitroso-N-methylurea
N-Nitroso-N-methylurethane
N-Nitrosomethylvinylamine
N-Nitrosomorpholine
N-Nitrosonornicotine
N-Nitrosopiperidine
Nitrosopyrrolidine
N-Nitrososarcosine
5-Nitro-o-toluidine
Octamethylpyrophosphoramide
Parathion
Pentachloronitrobenzene (PCNB)
Phenacetin
Phenylenediamine
2-Picoline
Pronamide
1,3-Propane sultone
n-Propylamine
Propylthiouracil
Saccharin and salts
Toluenediamine
o-Toluidine hydrochloride
Tolylene diisocyanate
Tris(1-azridinyl) phosphine sulfide
0,0-Diethyl S-methyl ester of phosphorodithioic acid
0,0-Diethylphosphoric acid, 0-p-nitrophenyl ester
Diisopropylfluorophosphate (DFP)
Dimethoate
Disulfoton
Hexaethyltetraphosphate
Phosphorodithioic acid, 0,0-diethyl S-((ethylthio)methyl) ester
Phosphorothioic acid, 0,0-dimethyl 0-(p-((dimethylamino)-sulfonyl)phenyl) ester

TABLE 7 - (Continued)

Tetraethyldithiopyrophosphate
Tetraethylpyrophosphate
0,0,0-Triethylphosphorothioate
Tris(2-3-dibromopropyl) phosphate

TABLE 8

Acetonitrile
Acrolein
Acrylamide
Acrylonitrile
1,2,3,4-diepoxybutane
*1,4-Dioxane
Ethylene oxide
Fromaldehyde
Glycidylaldehyde
Isobutyl alcohol
Methanethiol
Methyl ethyl ketone
Paraldehyde

*1,4-Dioxane cannot be eliminated by method 8630.

TABLE 9

Aflatoxins
Allyl alcohol
Azaserine
2-Butanone peroxide
Crotonaldehyde
Ethyl methacrylate
Ethyl methanesulfonate
Fluoroacetic acid
Formic acid
Malic anhydride
Methyl acetonitrile
Methyl methacrylate
Methyl methansulfonate
7-Oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid
Phenol
2-Propyn-1-ol
Streptozotocin
Tetranitromethane
Thiosemicarbazide
Thiourea

7.2 The procedure given in Figure 1 is the overall method. The analyst may need to add additional procedures into the overall scheme as necessary to identify specific components.

For example, suppose that Method 8600 indicates that a sample has high non-volatile TOX, is UV-active, and contains N/P compounds. Assuming that all of these effects are due to one compound entering the groundwater, the analyst may suspect the presence of one of the following compounds, especially if the analyst is aware that the facility which submitted the sample handles PCNB:

N,N Bis(2chloroethyl,-2-naphthylamine)
Diallate
3,3'-Dichlorobenzidine
4,4'-Methylenebis(2-chloroaniline)
Pentachloronitrobenzene (PCNB)

Since these are the only compounds which contain all of the indicated parameters, the analyst may wish to specifically analyze for these using other methods provided in this manual.

It should be clear that the one compound assumption is only a starting point for the analyst and does not mean that the analysis is finished if none of the five listed compounds are found. It is entirely possible that the observed effects could be due to three or more compounds.

7.3 There is a very large number of possible combinations and permutations of the available screening methods. The analyst may utilize them as necessary to determine sample composition.

7.4 Specific procedures to be followed in any of the 8600 methods are individually described in the sections in this manual dealing with each method.

8.0 Quality Control

8.1 Quality control procedures outlined in the individual methods used in Method 8600 should be followed.

9.0 Detection Limits

9.1 Detection limits for the analytical methods used in the 8600 series are individually described in each of the methods.

METHOD 8610

TOTAL AROMATICS BY ULTRAVIOLET ABSORPTION

1.0 Scope and Application

1.1 Method 8610 is designed to measure total aromatics present in extracts of groundwater samples by measuring the UV absorption of the sample relative to a background sample or a method blank. This method may be used with extracts of groundwater prepared by Method 3560.

1.2 Method 8610 is a screening method that may only be applied to groundwater samples as provided in Method 8600. The UV screening of groundwater samples is a simple, sensitive, and inexpensive method of determining which Appendix VIII compounds may be present in the sample.

1.3 This method may be used to determine the absence of the following compounds:

Polar UV Compounds

Acetophenone
3-(alpha-Acetonylbenzyl)-4-hydroxycomarin, and salts
2-Acetylaminoflourene
4-Aminobiphenyl
Mitomycin C
5-(Aminomethyl)-3-isoxazolol
Amitrole
Aniline
Aramite
Auramine
Benzenethiol
Benzidine
p-Benzoquinone
N,N-Bis(2-chloroethyl)-2-napthylamine
Bis(2-ethylhexyl) phthalate
Brucine
Butyl benzyl phthalate
2-sec-Butyl-2,4-dinitrophenol (DNBP)
Chlorambucil
p-Chloroaniline
Chlorobenzilate
p-Chloro-m-cresol
2-Chlorophenol
Citrus red No. 2
Coal tars
Creosote
Cresols

Polar UV Compounds (continued)

2-Cyclohexyl-4,-dinitrophenol
Daunomycin
Diallate
Di-n-butyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dichlorophenoxyacetic acid, salts and esters (2,4-D)
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester
Diethyl phthalate
Diethylstilbesterol
Dihydrosafrole
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol
3,3'-Dimethoxybenzidine
p-Dimethylaminoazobenzene
3,3'-Dimethylbenzidine
alpha,alpha-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethyl phthalate
Dinitrobenzene, N.O.S.
4,6-Dinitro-o-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
Diphenylamine
1,2-Diphenylhydrazine
Isosafrole
Maleic hydrazide
Methapyrilene
4,4'-Methylenebis(2-chloroaniline)
Methyl parathion
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
Nicotine and salts
p-Nitroaniline
Nitrobenzine
4-Nitrophenol
Parathion
Pentachloronitrobenzene (PCNB)
Pentachlorophenol
Phenacetin
Phenylenediamine
N-Phenylthiourea
Phosphorothioic acid, O,O-dimethyl O-(p((dimethylamino)-sulfonyl)phenyl) ester
Phthalic acid ester, N.O.S.
Phthalic anhydride

Polar UV Compounds (continued)

2-Picoline
Propylthiouracil
Pyridine
Reserpine
Resorcinol
Safrole
Strychnine and salts
Thioacetamide
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)
sym-Trinitrobenzene
Trypan blue
Uracil mustard

Non-Polar UV Compounds

Benz(c)acridine
Benz(a)anthracene
Benzene
Benzene, dichloromethyl-
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(a)pyrene
Benzotrichloride
Benzyl chloride
4-Bromophenyl phenyl ether
Chlorinated benzenes, N.O.S.
2-Chloronaphthalene
Chrysene
DDD
DDE
DDT
Dibenz(a,h)acridine
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
7H-Dibenzo(c,g)carbazole
Dibenzo(a,e)pyrene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
Dichlorobenzene, N.O.S.
7,12-Dimethylbenz(a)anthracene

Non-Polar UV Compounds (continued)

Fluoranthene
Heptachlor
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachlorophene
Idenol(1,2,3-cd)pyrene
Methoxychlor
3-Methylcholanthrene
Naphthalene
Polychlorinated biphenyls, N.O.S.
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

2.0 Summary of Method

2.1 The extracted groundwater sample is reduced (or made up) to a volume of 1 ml and transfered to a quartz cuvette.

2.2 A reagent blank or an upgradient groundwater sample is extracted with the sample and the UV region, 310 nm to 220 nm, is scanned for each sample versus the reagent blank or the upgradient sample.

Note: This Method can also be used over a wide range. If compounds which absorb in the visable range are expected the scan range should be extended to 700 nm to 220 nm.

3.0 Interferences

3.1 A procedural blank should be performed prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

4.0 Apparatus and Materials

4.1 Quartz cuvettes, with a 1 cm path length. Cuvettes with a 1 cc volume are recommended.

4.2 Double beam, adjustable slit, UV/VIS spectrophotometer capable of scanning the range 700 nm to 220 nm with a recording device.

4.3 Disposable pipets.

5.0 Reagents

5.1 Methanol: ACS spectrophotometric grade.

5.2 Hexane: ACS spectrophotometric grade.

6.0 Sample Collection and Preservation

6.1 Since this method may destroy some compounds in the sample, subsequent analysis should be performed on a fresh sample aliquot.

6.2 If the sample will be analyzed by additional methods the sample should be stored at 4°C prior to any additional analyses. Samples should be completely analyzed within 4 weeks of extraction.

7.0 Procedures

7.1 Place the groundwater extract into the quartz cuvette. The sample volume may be adjusted by either reducing the volume under a stream of nitrogen or increasing the volume with either hexane or methanol (use whichever is appropriate depending upon the fraction being analyzed).

7.2 Place the upgradient groundwater extract (or the method blank) into another quartz cuvette using the same procedure as in 7.1.

7.3 Place the upgradient (or method blank) sample into the reference sample holder of the UV spectrophotometer and place the sample (downgradient) into the test sample holder.

7.4 Scan the spectrophotometer in the constant intensity (variable slit mode) over the range of 310 nm to 220 nm and record the results. The scan should take at least 1 min.

7.5 After the scan is complete place the sample extract back into the sample vial it was taken from. Rinse the cuvette twice with a small amount of the solvent used and add the rinses to the sample vial.

7.6 Repeat steps 7.1 through 7.5 for the other (polar or non-polar) extract.

8.0 Quality Control

8.1 Analyze the spiked duplicates and the spiked reagent blanks to verify the sensitivity and detection limits.

8.2 The spiked samples should yield an absorbance of about .005 (99% transmittance) in the range of 270 to 300 nm.

9.0 Detection Limits

9.1 The detection limits for the spiked compounds are as follows:

Floranthene	0.3 ppb
Parathion	4.0 ppb
Trichlorophenol	4.0 ppb

9.2 Detection limits for Appendix VIII compounds will vary depending on molar absorbtivity coefficiences. For example, the spiked reagent blank will contain 25 ng of Floranthene in 1 ml of hexane (λ_{max} = 286 nm; Σ = 45000). Therefore the absorbance will be

$$A = \frac{45000\ \lambda}{\text{cin-mole}}\ 1\ \text{cm} \cdot 1.24 \times 10^{-7}\ \text{moles/liter}$$

$$A = .0056$$

The cut-off used in deciding whether a compound was UV active was molar absorbtivity coefficient of 1000 or higher. Therefore a compound with a molecular wt of 250 gm/mole can first be detected at a level of:

$$.005 = \frac{1000\ 1}{\text{cin-mole}}\ 1\ \text{cm}\ x\ \text{moles/liter}$$

$$x = 5 \times 10^{-6}\ \text{mole/l}$$

$$5 \times 10^{6}\ \text{moles/l} \cdot 250\ \text{gm/mole} = 1250 \times 10^{-6}\ \text{gm/liter}$$

$$= 1.25\ \text{mg/l}$$

Since we concentrated the sample 100:1 the detection limit of this method should be at least 12.5 ppb for all of the compounds listed.

10.0 Pass/Fail Criteria

10.1 The Pass/Fail criteria for groundwater samples determined using method 8610 is straight forward and utilizes the background correction supplied by the upgradient sample.

10.2 Since the up gradient sample is placed in the reference cell any absorption due to indigenous UV active compounds should be automatically subtracted out.

10.3 A ground water sample will fail method 8610 if the sample absorbs more than .005 absorbance units in the range from 310 nm to 220 nm.

METHOD 8620

TOTAL NITROGEN-PHOSPHORUS GAS CHROMATOGRAPHABLE COMPOUNDS

1.0 Scope and Application

1.1 Method 8620 is used to determine the absence (and in some cases the presence) of certain nitrogen- or phosphorus-containing Appendix VIII compounds in groundwater samples. Specifically Method 8620 can be used to detect the following substances:

Non-Polar

Dibenz(a,h)acridine
Dibenz(a,j)acridine
7H-Dibenzo(c,g)carbazole

Polar

1-Acetyl-2-thiourea
4-Aminobiphenyl
5-(Aminomethyl)-3-isoxaxolol
Amitrole
Aniline
Auramine
Benzidine
N,N-Bis(2-chloroethyl)-2-naphthylamine
Brucine
2-sec-Butyl-2,4-dinitrophenol (DNBP)
3-Chloropropionitrile
2-Cyclohexyl-4,6-dinitrophenol
Cyclophosphamide
Diallate
3,3'-Dichlorobenzidine
N,N-Diethylhydrazine
O,O-Diethyl O-2-pyrazinyl phosphorothioate
Dimethoate
3,3'-Dimethoxybenzidine
p-Dimethylaminoazobenzene
3,3'-Dimethylbenzidine
1,1-Dimethylhydrazine
1,2-Dimethylhydrazine
3,3-Dimethyl-1-(methylthio)-2-butanone
alpha,alpha-Dimethylphenethylamine
Dinitrobenzene, N.O.S.

- .

Polar Compounds (continued)

4,6-Dinitro-o-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Diphenylamine
1,2-Dipehnylhydrazine
Di-n-propylnitrosamine
2,4-Dithiobiuret
Ethyl carbamate
Ethyl cyanide
Ethyleneimine
Ethylenethiourea
Hydrazine
Maleic hydrazide
Malononitrile
Methapyrilene
Metholmyl
2-Methylaziridine
4,4'-Methylenebis(2-chloroaniline)
2-Methylactonitrile
2-Methyl-2-(methylthio)propionaldehyde-o-(methyl carbonyl)oxime
N-Methyl-N'-nitro-N-Nitrosoquanidine
Methyl parathion
Methylthiouracil
1-Naphthylamine
2-Naththylamine
1-Naphthyl-2-thiourea
Nicotine and salts
p-Nitroaniline
Nitrobenzine
Nitroglycerin
4-Nitrophenol
4-Nitroquinoline-1-oxide
Nitrosamine, N.O.S.
N-Nitrosodi-n-butylamine
N-Nitrosodiethanolamine
N-Nitrosoliethylamine
N-Nitrosodimethylamine
N-Nitroso-N-ethylurea
N-Nitrosomethylethylamine
N-Nitroso-N-methylurea
N-Nitroso-N-methylurethane
N-Nitrosomethylvinylamine
N-Nitrosomorpholine
N-Nitrosonornicotine
N-Nitrosopiperidine
Nitrosopyrrolidine

Polar Compounds (continued)

N-Nitrososarcosine
5-Nitro-o-toluidine
Octamethylpyrophosphoramide
Parathion
Pentachloronitrobenzene (PCNB)
Phenacetin
Phynylenediamine
2-Picoline
Pronamide
1,3-Propane sultone
n-Propylamine
Propylthiouracil
Saccharin and salts
Toluenediamine
o-Toluidine hydrochloride
Tolylene diisocyanate
Tris(1-azridinyl) phosphine sulfide
0,0-Diethyl S-methyl ester of phosphorodithioic acid
0,0-Diethylphosphoric acid, 0-p-nitrophenyl estr
Diisopropylfluorophosphate (DFP)
Disulfoton
Hexaethyltetraphosphate
Octamethylpyrophosphoramide
Phosphorodithioic acid, 0,0-diethyl S-(ethylthio)methl) ester
Phosphorothioic acid, 0,0-dimethyl 0-(p-((dimethylamino)-sulfonyl) phenyl)ester
Tetraethyldithiopyrophosphate
Tetraethylpyrophosphate
0,0,0-Triethylphosphorothioate
Tris(2,3-dibromopropyl) phosphate

1.2 This method is intended to be used as a screening technique for the compounds listed in 1.1. Potential identification and quantitation of specific components can be accomplished by comparison of retention time and area response to authentic standards.

2.0 Summary of Method

2.1 Method 8260 provides capillary column gas chromatographic conditions for screening for the compounds listed in Section 1.1 at the parts per billion (ppb) level using a N/P type detector. Prior to the use of this method, groundwater samples are extracted using Method 3560.

2.2 Spiked samples, upgradient samples, and reagent blanks are used to determine whether any of the compounds of interest are present.

2.3 This method is used as part of an overall screening technique described in Method 8600. Prior to using this method analysts should familiarize themselves with this overall screening method.

3.0 Interferences

3.1 Matrix interferences may be caused by contaminants which are coextracted from the sample. The extent of matrix interference will vary considerably from sample to sample. However, this is partially addressed by processing upgradient groundwater samples at the same time and comparing the chromatograms obtained.

4.0 Apparatus and Materials

4.1 Gas chromatograph: Analytical system complete with gas chromatograph with on-column capillary injection system. (SGE "OCI-3" or equivalent injector can be used to retrofil existing gas chromatographs). Required accessories are syringes, gases, detector, and strip chart recorder or data system.

4.2 Column: 15 m wall coated open tubular column .25 mm id silicone phase (SE30, SE54, DB5, etc.).

4.3 Detector: Nitrogen/Phosphorus (N/P).

5.0 Reagents

5.1 Hexane: ACS spectrophotometric grades.

5.2 Methanol.

6.0 Sample Handling and Preservation

6.1 Sample extracts (1 ml) obtained by Method 3560 which have been stored at 4°C may be analyzed directly by this method.

6.2 After analysis the remaining sample should be stored at 4°C in its original vial for future analysis.

6.3 All samples should be completely analyzed within 4 weeks of extraction.

7.0 Procedure

7.1 The recommended gas chromatographic operating conditions are:

7.1.1 Helium carrier gas with a linear velocity of 30 cm/sec.

7.1.2 Inject (Using on-column splitless method) at 45°C and hold for 2 min. Program to 270°C at 6°/min and hold at 270°C for 15 min. Inject at 35°C.

7.2 Inject 2 µl of the polar fraction of the spiked blank sample obtained from Method 3560 onto the column. Adjust the attenuation to give approximately half scale deflection for the parathion peak.

7.3 Verify that parathion is detected and that the quantity injected is .8 ng (± 20%) using an external calibration injection of .8 ng parathion.

7.4 Analyze both the hexane and methanol fractions of the upgradient and downgradient ground water samples.

7.5 Analyze the QC extract samples (spiked duplication) blanks, and spiked blanks with each set of samples as provided in Method 3560.

8.0 Quality Control

8.1 Before processing any samples the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference free.

8.2 The analyst must verify that the recovery of parathion from duplicate spikes and blank spikes is at least 80% (see 7.3) before analysis of any other samples.

9.0 Detection Limits

9.1 The estimated detection limit of this method is .1 ng for parathion.

10.0 Pass/Fail Criteria

10.1 The Pass/Fail criteria employed in Method 8620 involves 3 cases. The first case, which should be encountered most frequently, results when no peaks (compounds) are detected in the upgradient sample. In this instance any peaks found in the downgradient sample will constitute a failed test. The second case is encountered when the same peaks are present in both the upgradient and downgradient samples. In this case, the analyst will compare the areas (or peak heights) of the peaks from both chromatograms. If any downgradient peak is greater than 2 times the upgradient, the sample fails. The final case will be when peaks are detected both in the upgradient and downgradient but the downgradient sample contains more peaks. This situation is also a failure. Instrument sensitivity for Method 8620 is set by injecting 0.8 ng of parathion and adjusting the attenuation for half scale deflection (peaks less than 5% full scale may be ignored).

METHOD 8630

DERIVATIZATION PROCEDURE FOR APPENDIX VIII COMPOUNDS

1.0 Scope and Application

1.1 Method 8630 is used to derivatize certain Appendix VIII compounds which are part of Method 8600 hierarchial scheme. Method 8630 may also be used to form derivatives for both gas chromatography electron capture and mass spectrometry detection.

1.2 Specifically this method may be used to determine the presence or absence of the following compounds:

Acetonitrile
Acetophenone
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin, and salts
2-Acetylaminofluorene
Acetyl chloride
1-Acetyl-2-thiourea
Acrolein
Acrylamide
Acrylonitrile
Aflatoxins
Allyl alcohol
4-Aminobiphenyl
Mitomycin C
5-(Aminomethyl)-3-isoxazolol
Amitrole
Aniline
Aramite
Auramine
Azaserine
Benzenethiol
Benzidine
p-Benzoquinone
Bis(2-ethylhexyl) phthalate
Bromoacetone
Brucine
2-Butanone peroxide
Butyl benzyl phthalate
2-sec-Butyl-2,4-dinitrophenol (DNBP)
Chloral
Chlorambucil
Chlorinated phenol, N.O.S.
Chloroacetaldehyde

p-Chloroaniline
Chlorobenzilate
p-Chloro-m-cresol
1-Chloro-2,3-epoxypropane
2-Chlorophenol
1-(o-Chlorophenyl)thiourea
3-Chloropropionitrile
Citrus red No. 2
Coal tars
Creosote
Cresols
Crotonaldehyde
Cycasin
2-Cyclohexyl-4,6-dinitrophenol
Cyclophosphamide
Daunomycin
Diallate
Di-n-butyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dichlorophenoxyacetic acid, salts and esters (2,4-D)
Dichloropropanol, N.O.S.
1,2:3,4-Diepoxybutane
N,N-Diethylhydrazine
O,O-Diethyl S-methyl ester of phosphorodithioic acid
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester
Diethyl phthalate
O,O-Diethyl O-2-pyrazinyl phosphorothioate
Diethylstilbesterol
Dihydrosafrole
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol
Diisopropylfluorophosphate (DFP)
Dimethoate
3,3'-Dimethoxybenzidine
p-Dimethylaminoazobenzene
3,3'-Dimethylbenzidine
Dimethylcarbamoyl chloride
1,1-Dimethylhydrazine
1,2-Dimethylhydrazine
3,3-Dimethyl-1-(methylthio)-2-butanone
alpha,alaph-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethyl phthalate
Dinitrobenzene, N.O.S.
4,6-Dinitro-o-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene

Di-n-octyl phthalate
Diphenylamine
1,2-Diphenylhydrazine
Di-n-propylnitrosamine
Disulfoton
2,4-Dithiobiuret
Endosulfan
Endrin and metabolites
Ethyl carbamate
Ethyl cyanide
Ethylenebisdithiocarbamic acid, salts and esters
Ethyleneimine
Ethylene oxide
Ethylenethiourea
Ethyl methacrylate
2-Fluoroacetamide
Fluoroacetic acid, sodium salt
Formaldehyde
Formic Acid
Glycidylaldehyde
Hexaethyltetraphosphate
Hydrazine
Isocyanic acid, methyl ester
Isobutyl alcohol
Isosafrole
Lasiocarpine
Maleic anhydride
Maleic hydrazide
Malononitrile
Melphalan
Methacrylonitrile
Methanethiol
Metholmyl
2-Methylaziridine
4,4'-Methylenebis(2-chloroaniline)
Methyl ethyl ketone (MEK)
Methyl hydrazine
2-Methyllactonitrile
Methylmethacrylate
2-Methyl-2-(methylthio)propionaldehyde-o-(methylcarbonyl) oxime
N-Methyl-N'-nitro-N-Nitrosoguanidine
Methyl parathion
Methylthiouracil
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
1-Naphthyl-2-thiourea
p-Nitroaniline

Nitrobenzine
Nitroglycerin
4-Nitrophenol
4-Nitroquinoline-1-oxide
Nitrosamine, N.O.S.
N-Nitrosodi-n-butylamine
N-Nitrosoldiethanolamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
N-Nitroso-N-ethylurea
N-Nitrosomethylethylamine
N-Nitroso-N-methylurea
N-Nitroso-N-methylurethane
N-Nitrosomethylvinylamine
N-Nitrosomorpholine
N-Nitrosonornicotine
N-Nitrosopiperidine
Nitrosopyrrolidine
N-Nitrososarcosine
5-Nitro-o-toluidine
Octamethylpyrophosphoramide
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid
Paraldehyde
Parathion
Pentachloronitrobenzene (PCNB)
Pentachlorophenol
Phenacetin
Phenol
Phenylenediamine
N-Phenylthiourea
Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester
Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)-sulfonyl)
    phenyl) ester
Phthalic acid esters, N.O.S.
Phthalic anhydride
Pronamide
n-Propylamine
Propylthiouracil
2-Propyn-1-ol
Reserpine
Resorcinol
Saccharin and salts
Safrole
Streptozotocin
Strychnine and salts
2,3,4,6-Tetrachlorophenol

Tetraethyldithiopyrophosphate
Tetraethylpyrophosphate
Tetranitromethane
Thioacetamide
Thiosemicarbazide
Thiourea
Thiuram
Toluenediamine
o-Toluidine hydrochloride
Tolylene diisocyanate
Trichloromethanethiol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
2,4,5-Trichlorophenoxypropionic acid)2,4,5-TP)
0,0,0-Triethylphosphorothioate
sym-Trinitrobenzene
Tris(1-azridinyl) phosphine sulfide
Tris(2-3-dibromopropyl) phosphate
Trypan blue
Uracil mustard

2.0 Summary of Method

2.1 Aqueous samples are prepared using method 3560 using diethylether as the eluting solvent.

2.2 Ether extracts are dried over sodium sulfate and then reacted with litium aluminum hydride.

2.3 Compounds are then hydrolized to their parent alcohols or aminos by adding a small amount of water and then the dinitrophenyl esters are formed by adding 3,5 dinitrobenzyl chloride.

2.4 Excess benzyl chloride is removed by adding water and washing with base. Derivatives are extracted into methylene chloride and subjected to Method 8610 to determine the presence of Appendix VIII compounds.

3.0 Interferences

3.1 A procedural blank should be performed prior to the use of this method. The level of interferences must be below the method detection limit before this method is used on actual samples.

4.0 Apparatus and Materials

4.1 Reacti-Vials, 5-ml, Pierce 13223 or equivalent.

4.2 Separatory funnel, 25-ml.

4.3 Syringe, 100-µl.

4.4 Realti-Therm system, Pierce 18900 and 18780 or equivalent.

5.0 Reagents

5.1 Lithium aluminum hydride.

5.2 Diethylether: ACS reagent grade.

5.3 3,5 dinitrobenzoylchloride.

5.4 Distilled, dionized water.

5.5 Sodium sulfate; dried at 400°C.

6.0 Sample Collection and Preservation

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

6.2 After extraction of samples by this method, diethylether extracts may be stored at 4°C prior to analysis. Sample extracts should be analyzed as soon as possible after extraction and should not exceed 4 weeks after extraction.

7.0 Procedure

7.1 Prepare a fresh groundwater sample using method 3560 using Diethylether as the eluting solvent.

7.2 Do not concentrate the ether extract. Transfer about 2.5 ml of the extract to a 55-ml reacti-vial. Dry the ether by adding about .5 gm Na_2SO_4 and shake.

7.3 Remove the supernate to a clean 5-ml reacti-vial.

7.4 Add 100 µl of a 1M solution of $LiAlH_4$ in diethylether and mix on a vortex shaker. Place reacti-vial in reacti-therm and heat at 60°C for 1 hr.

7.5 Add 100 µl water and shake on vortex mixer.

7.6 Add 200 µl of 1M solution of 3,5 dinitrobenzoyl chloride, shake and return to reacti-therm at 60°C for 1 hr.

7.7 Add 1 ml water that had been adjusted to pH 9 with NaOH.

7.8 Shake the vial on a vortex shaker and allow phases to separate. Carefully remove the water layer with a disposable pipet.

7.9 Repeat step 7.8 twice more.

7.10 Concentrate the ether layer using nitrogen and reacti-therm system and proceed to Method 8610 scanning from 700 nm to 220 nm for detection of groundwater contaminants.

8.0 Quality Control

8.1 Every 10th sample, or at least one sample in each set of samples, should be a spiked duplicate. The sample should be spiked with 4 µg of phenol.

8.2 Before processing any samples the analyst should demonstrate the absence of interferences through the analysis of a diethylether reagent blank.

9.0 Detection Limits

9.1 The UV/VIS detection limits for the 3,5 dinitrobenzoate of most alcohols (or the corresponding amide) is approximately 4 ppb.

10.0 Pass/Fail Criteria

10.1 The Pass/Fail criteria for groundwater samples determined using method 8610 is straight forward and utilizes the background correction supplied by the upgradient sample.

10.2 Since the upgradient sample is placed in the reference cell any absorption due to indigenous UV active compounds should be automatically subtracted out.

10.3 A groundwater sample will fail Method 8610 if the sample absorbs more than .005 absorbance units in the range from 310 nm to 220 nm.

METHOD 9011

Method for the Determination of Photodegradable Cyanides

1.0 Scope and Application

1.1 Method 9011 is used for the determination of photodegradable cyanides in wastes under hypothetical field conditions. It is used to determine whether particular wastes will form releasable cyanides (cyanide amenable to chlorinate) as a result of exposure to UV radiation.

2.0 Summary of Method

2.1 Four representative waste samples are tested. Each sample is split into two equal portions. One portion is subjected to UV irradiation by a low pressure mercury arc lamp to test for photodegradation. During irradation, any HCN evolved is trapped in the gas absorber. After photolysis is completed, each portion is analyzed according to method 9010. The presence of photodegradable cyanides is determined by the differences in results.

3.0 Interferences

3.1 Refer to Method 9010

4.0 Apparatus and Materials

4.1 Quartz tube, (1.26 cm I.D. x 15 cm, "Vycor" brand from corning, or 11-369E in Fisher catalogue) with provision for air inlet and vacuum outlet, transparent to UV frequencies greater than 220nm.

4.2 Low pressure mercury lamp (G15T8 lamp, General Electric or equivalent capable of emitting UV radiation at a frequency below 300nm).

4.3 Microburet; refer to Method 9010.

4.4 Flasks, condenser, and tubing are needed as shown in Figure 1. The boiling flask should be of 1-liter size with inlet tube and provision for a condenser. The gas absorber may be a Fisher-Milligan scrubber. Assemble as shown in Figure 1.

5.0 Reagents

5.1 Refer to Method 9010.

6.0 Sample Collection, Preservation and Handling

6.1 Refer to Method 9010.

7.0 Procedure

7.1 Test for interferencs according to the procedure in Method 9010.

7.2 Take a 20 gram sample of waste and split into two 10 gram portions.

7.3 Analyze one portion (A) for total and amenable cyanide according to Method 9010.

7.4 Take the second 10 gram portion (B) of the sample and place in a quartz tube.

7.4.1 Connect quartz tube inlet to an air source and the tube outlet to the adsorber as specified in procedure 7.3 in Method 9010.

7.4.2 Using the mercury arc lamp at a distance of twelve inches from the quartz tube, irradiate for thirty minutes while drawing air through the system.

Caution: Low pressure mercury arc lamps emit high energy ultraviolet radiation. Use caution to avoid exposing eyes or skin.

7.4.3 Determine the presence of total and amenable cyanide according to procedures 7.3 - 7.5 in Method 9010 on the sample in the quartz tube.

7.4.4 Determine the amount of CN in the scrubber.

7.5 Report results for the five measurements from each sample.

EXAMPLE:

CN in ppm

	Total	Cn Amenable	Scrubber
Sample 1A	82.5	10.4	--
Sample 1B	63.1	21.8	5.7

This example would result from a sample which converted complexed cyanide to amenable.

7.6 Spiked standards and check standards should be routinely analyzed.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference and inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences.

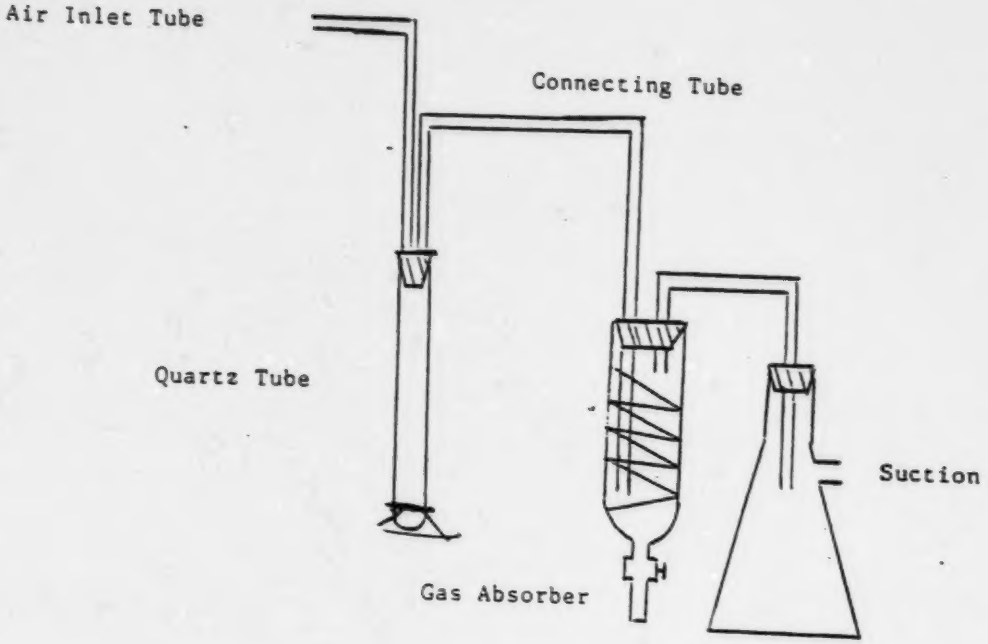

Air Inlet Tube
Connecting Tube
Quartz Tube
Suction
Gas Absorber

Figure 1. Apparatus for Cyanide Distillation

METHOD 9022

TOTAL ORGANIC HALIDES (TOX) BY NEUTRON ACTIVATION ANALYSIS

1.0 Scope and Application

1.1 Method 9022 determines Total Organic Halides (TOX) in drinking, ground, and river waters, and in wastewater treatment plant effluents. The method uses a carbon adsorption procedure identical to that of Method 9020 (TOX analysis using a microcoulometric-titration detector), irradiation by neutron bombardment, then detection using a gamma-ray detector. The reliable limits of detection are 5 ppb for chlorine and 1 ppb for iodine and bromine.

1.2 Method 9022 detects all organic halides containing chlorine, bromine, iodine, and fluorine that are adsorbed by granular activated carbon under the conditions of the method. Each halogen can be quantitated independently.

1.3 Method 9022 is restricted to use by, or under the supervision of, analysts experienced in the operation of neutron activation analysis and familiar with spectral interferences.

1.4 This method may be used in place of Method 9020 and has the advantage of determining the individual concentrations of the halogens chlorine, bromine, and iodine in addition to TOX.

2.0 Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of granulated activated carbon (GAC). The column is washed to remove any trapped inorganic halides. The GAC sample is exposed to thermal neutron bombardment creating a radioactive isotope. Gamma-ray emission, which is unique to each halogen, is counted. The area of the resulting peaks is directly proportional to the concentration of the halogens.

3.0 Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution.

This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400° C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 2000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 It is possible that other radioisotopes, stray radiation, counting geometries, and counting-equipment materials can affect gamma counting. It is essential that the data interpretation be performed by an analyst experienced at detecting these interferences.

4.0 Apparatus and Materials

4.1 Adsorption system

4.1.1 Dohrmann adsorption module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.1.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 2000 ng Cl^- equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville), or equivalent: Form this material into plugs using a 2-mm-I.D. stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

4.1.5 Column holders (available from Dohrmann).

4.1.6 Volumetric flasks: 100-ml, 50-ml. A general schematic of the adsorption system is shown in Figure 1.

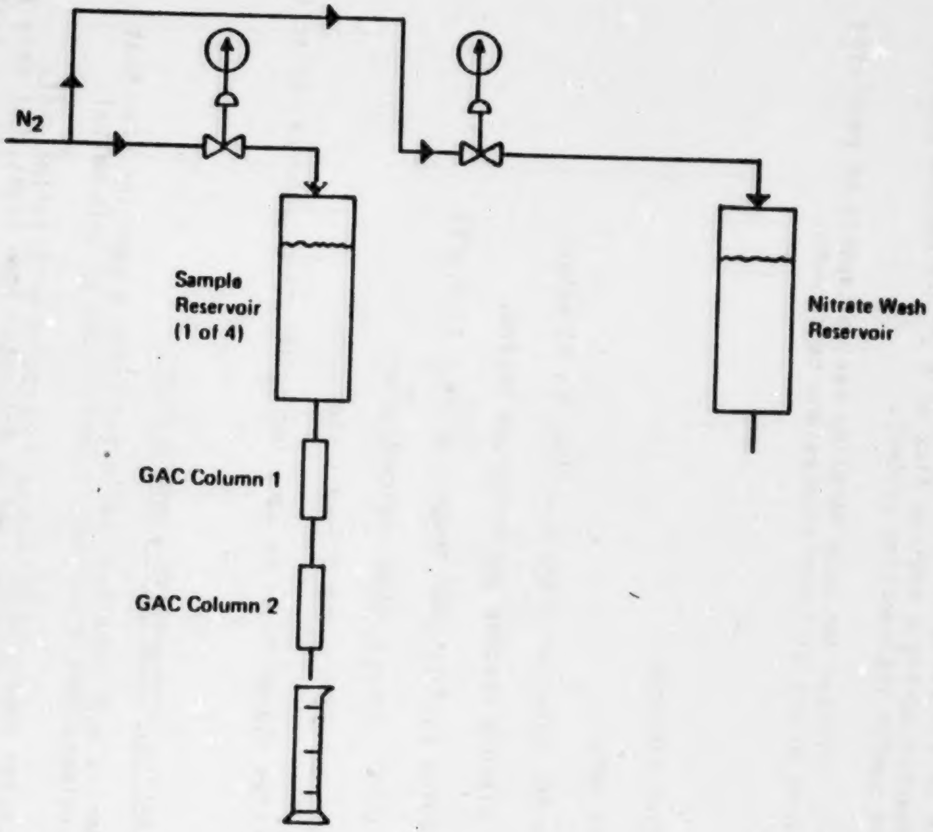

N2
Sample Reservoir (1 of 4)
Nitrate Wash Reservoir
GAC Column 1
GAC Column 2

Figure 1. Schematic of Adsorption System.

4.2 Containers suitable for containment of samples and standards during irradiation (e.g., 1/5-dram polyethylene snap-cap vial).

4.3 Sample introduction system and a reactor generating a thermal neutron flux capable of achieving enough halogen activity for counting purposes (e.g., a reactor having a neutron flux of 5 x 10^{12} neutrons/cm^2/sec and a pneumatic-tube sample introduction system).

4.4 A gamma-ray detector and data handling system capable of resolving the halogen peaks from potential interferences and background.

5.0 Reagents

5.1 Prepurified nitrogen.

5.2 Deionized water.

5.3 5000 ppm NO_3 solution (KNO_3 dissolved in DI water).

5.4 50% v/v mixture acetone and nanograde hexane.

5.5 0.1 M sodium sulfite (ACS reagent grade - 12.6 g/l).

5.6 Nitric acid: concentrated, reagent grade.

5.7 25-µg Cl, 2.5-µg Br, and 2.5-µg I standards.

5.8 Radioactive standards to be used for calibrating gamma-ray detection systems.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples should be collected in bottles with teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass, 250-ml, fitted with teflon-lined caps. Foil may be substituted for teflon if the sample is not corrosive. Samples must be protected against loss of volatiles by eliminating headspace in the container. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400° C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in 3.1.1.

7.0 Procedure

7.1 Sample preparation

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on the front and back columns.

7.1.2 Reduce residual chlorine by adding sulfite (1 ml of 0.1 M per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4° C without headspace.

7.1.3 Adjust the pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

7.2 Calibration

7.2.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 ml of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight analysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then analyze the carbon.

7.2.3 Prior to each day's operation, the instrument is calibrated using radioactive standards (e.g., cobalt-60 and radium-226 sources). The instrument is calibrated such that gamma rays from the standards fall within plus or minus one channel of their true energies. A 100-sec blank is then counted to verify that no stray radioactive sources are within sensing distance of the detector. As data are obtained throughout the day peak locations in the standards are monitored to ensure there is no electronic drift of the instrument. If drift is noted, the system is recalibrated.

7.3 Adsorption procedure

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately

3 ml/min. NOTE: 100 ml of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/l; 50 ml for 501 to 1000 g/l, and 25 ml for 1001 to 2000 g/l.

7.3.3 Wash the columns-in-series with at least 2 ml of the 5000-mg/l nitrate solution at a rate of approximately 2 ml/min to displace inorganic chloride ions.

7.4 Activation

7.4.1 After the quartz collection tube with the GAC is removed from the extraction unit, the GAC and cerafelt pads are extruded using the packing rod into a prewashed plastic container (e.g., 1/5-dram polyethylene snap-cap vial). The vial is prewashed to remove inorganic and organic chorine by soaking in distilled water followed by storage in a glass jar containing 50% v/v acetone and hexane. Just prior to extrusion the vial is removed by forceps and air-dried to remove residual water, acetone, and hexane. The vial is snapped shut, the hinge removed with a scalpel blade, the cap heat-sealed to the vial with an electric soldering gun reserved for that purpose, and a single-digit number placed on the vial with a Marks-A-Lot (or equivalent) marker pen.

7.4.2 Samples plus a similar vial containing 25 µg Cl, 2.5 µg Br and 2.5 µg I standards are then introduced into the reactor, generally by placing them together in a 5-dram polyethylene vial and inserting them into a pneumatic-tube transfer "rabbit" for neutron irradiation. Irradiation would be for a 15-min period at a thermal neutron flux of 5 x 10^{12} neutrons/cm^2/sec. After returning from the reactor the rabbit is allowed to "cool" for 20 min to allow short-lived radioisotopes (primarily Al) present in the GAC to decay away.

7.5 Detection

7.5.1 Analysis is performed using lithium drifted germanium Ge(Li) gamma ray detector with an amplifier and a 4096-channel memory unit for data storage. The analyses can be performed either manually, with the operator changing samples and transferring the data to magnetic tape, or automatically, with both functions performed by an automatic sample changer.

7.5.2 Analysis begins by counting the standard and samples for a suitable time period (e.g., 200 sec "live" time for the standards and samples). The operator records the time intervals between samples and the "dead" time of each sample in a logbook for later use in calculating halogen concentrations in each sample.

7.6 Calculations

7.6.1 Chlorine, bromine, and iodine can be analyzed within a 200-sec counting period taking place 20 to 40 min after irradiation.

7.6.2 Chlorine is analyzed using the 1642-KeV gamma ray produced by 37.1-min ^{38}Cl. Bromine is analyzed using the 616-KeV gamma ray from 17.7-min ^{80}Br, while iodine is analyzed using the 442-KeV gamma ray produced by 25-min ^{128}I.

7.6.3 The calculation used for quantitation is:

$$\text{ppm halogen} = \frac{\text{cts unk.}}{\text{cts std.}} \times \frac{\text{counting time std.}}{\text{counting time unk.}} \times \frac{\mu\text{g in std.}}{\text{sample vol.}} \times e^{\lambda t}$$

where

cts unk. = the integrated area of the appropriate gamma-ray peak in the unknown with background subtracted and the total multiplied by 1 + [(% dead time unknown - % dead time std.)/200]. The latter correction is usually less than 4% and corrects for pile-up errors.

cts std. = the integrated area of the appropriate gamma-ray peak in the standard with background subtracted.

counting time std. = the "live" counting time in seconds of the standard.

counting time unk. = the "live" counting time in seconds of the unknown.

μg in std. = the number of micrograms of the stable element in question in the standard (25 for Cl, 2.5 for Br and I).

sample vol. = the volume of sample passed through the GAC column, in milliliters.

$e^{\lambda t}$ = The decay correction to bring all statistics back to $t = 0. \lambda = 0.693/t_{1/2}$ where $t_{1/2}$ = the half-life, in minutes.

t = the time interval in minutes from the end of the count of the standard until the end of the count of the sample.

7.6.4 No further calculations are necessary as long as the final sample is counted within 40 min after the end of irradiation. If samples are counted after 40 min, the addition to the 616-KeV peak of ^{80}Br from the 619-KeV peak from ^{82}Br becomes large enough that a correction factor must be applied. In practice all counting should be completed in less than 40 min after irradiation.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by analyzing appropriate quality-control check samples.

8.3 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

8.4 Employ a minimum of one blank per sample batch to determine if contamination is occurring.

8.5 Run check standard after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

8.8 Quality control for the analysis phase is very straightforward since the instrument is a noncontact analyzer. That is, only the radiation emitted from the sample - not the sample itself - should touch the analyzer. Since contamination of the system is not usually a problem (unless a sample spills on it), the most serious quality-control issues deal with uniform neutron flux, counting geometry, and spectral interpretation. The amount of radioactivity induced in a sample is directly proportional to the neutron flux it is exposed to. Since this flux can vary depending on how the sample is positioned in relation to the reactor core during irradiation, it is essential that a known standard be irradiated with every sample batch to act as a flux monitor. Care must also be taken to ensure that the standard and all samples associated with the standard are counted at the same distance from the detector.

METHOD 9035

SULFATE (COLORIMETRIC, AUTOMATED, CHLORANILATE)

1.0 Scope and Application

1.1 This automated method is applicable to ground, drinking and surface waters, and domestic and industrial wastes containing 10 to 400 mg SO_4/liter. Approximately 15 samples per hour can be analyzed.

2.0 Summary of Method

2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid solution is proportional to the amount of sulfate present.

3.0 Interferences

3.1 Cations, such as calcium, aluminum, and iron, interfere by precipitating the chloranilate. These ions are removed by passage through a cation exchange column.

3.2 The continuous filters are readily contaminated and difficult to work with.

4.0 Apparatus

4.1 Technicon AutoAnalyzer consisting of:

4.1.1 Sampler I.

4.1.2 Continuous filter.

4.1.3 Manifold.

4.1.4 Proportioning pump.

4.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.

4.1,6 Recorder.

4.1.7 Heating bath, 45° C.

4.2 Magnetic stirrer.

5.0 Reagents

5.1 Barium chloranilate: Add 9 g of barium chloranilate ($BaC_6Cl_2O_4$) to 333 ml of ethyl alcohol and dilute to 1 liter with distilled water.

5.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 ml of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.

5.3 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g EDTA in distilled water and dilute to 1 liter. This solution is also used to clean out the manifold system at end of sampling run.

5.4 Ion exchange resin: Dowex-50 W-X8, ionic form-H^+. The column is prepared by sucking a slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.

5.5 Stock solution: Dissolve 1.4790 g of oven-dried (105° C) Na_2SO_4 in distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg.

5.6.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Refrigerate at 4° C.

7.0 Procedures

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated $BaSO_4$ and the unused barium chloranilate are removed by filtration. If any $BaSO_4$ should come through the filter, it is complexed by the NaOH-EDTA reagent).

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

7.6 Calculation

7.6.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

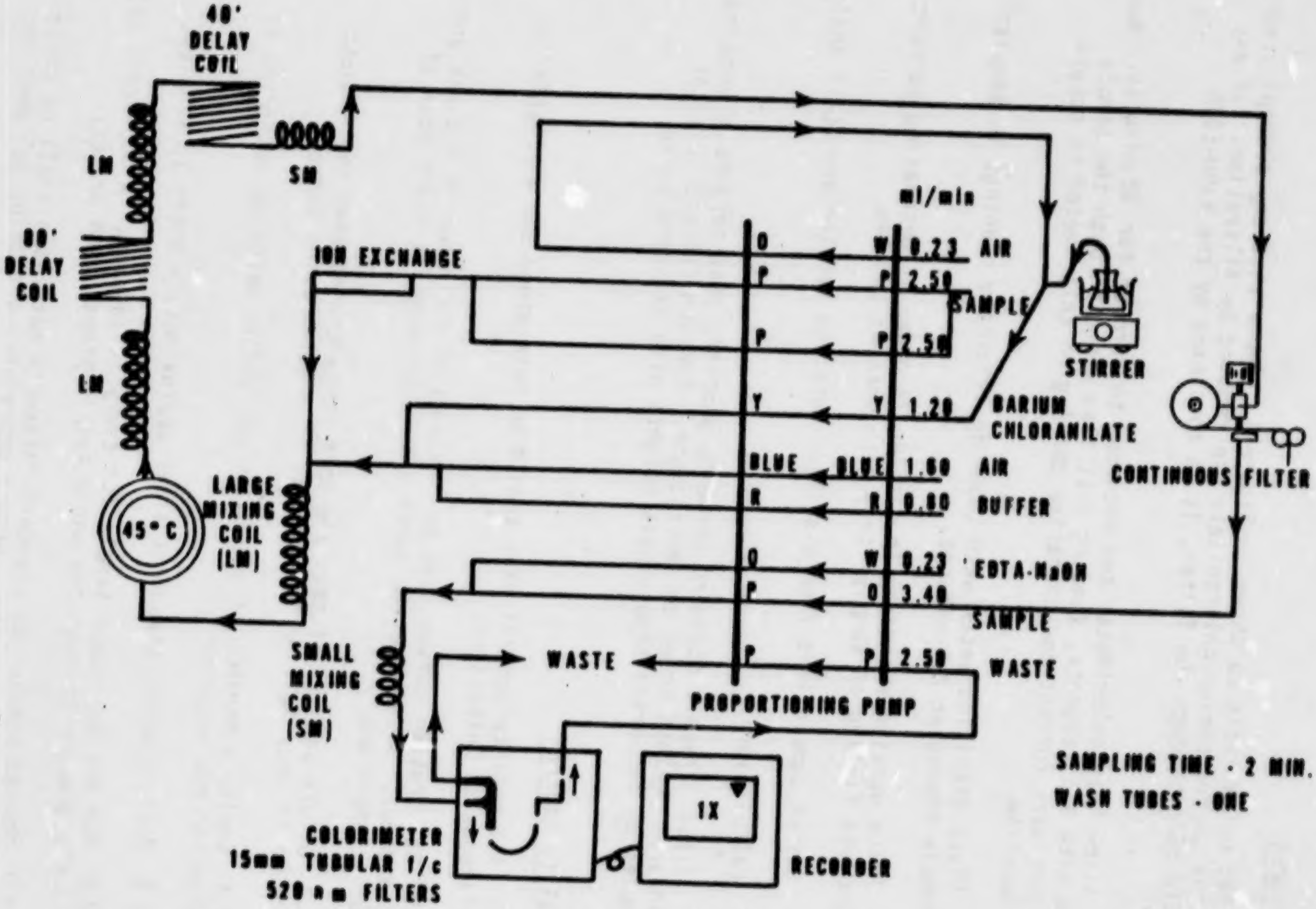
8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.


40' DELAY COIL
LM
SM
80' DELAY COIL
LM
45° C
LARGE MIXING COIL (LM)
ION EXCHANGE
ml/min
O
P
P
Y
BLUE
R
O
P
P
W 0.23 AIR
P 2.50 SAMPLE
P 2.50
Y 1.20 BARIUM CHLORANILATE
BLUE 1.60 AIR
R 0.80 BUFFER
W 0.23 EDTA-NaOH
O 3.40 SAMPLE
P 2.50 WASTE
STIRRER
CONTINUOUS FILTER
WASTE
PROPORTIONING PUMP
SMALL MIXING COIL (SM)
COLORIMETER 15mm TUBULAR f/c 520 n m FILTERS
1X
RECORDER

SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - SULFATE MANIFOLD AA-I

METHOD 9036

SULFATE (COLORIMETRIC, AUTOMATED, METHYLTHYMOL BLUE, AA II)

1.0 Scope and Application

1.1 This automated method is applicable to ground, drinking, and surface waters, and domestic and industrial wastes.

1.2 Samples in the range of 0.5 to 300 mg SO_4/liter can be analyzed.

2.0 Summary of Method

2.1 The sample is first passed through a sodium form cation-exchange column to remove multivalent metal ions. The sample containing sulfate is then reacted with an alcohol solution of barium chloride and methylthymol blue (MTB) at a pH of 2.5-3.0 to form barium sulfate. The combined solution is raised to a pH of 12.5-13.0 so that excess barium reacts with MTB. The uncomplexed MTB color is gray; if it is all chelated with barium, the color is blue. Initially, the barium and MTB are equimolar and equivalent to 300 mg SO_4/liter; thus the amount of uncomplexed MTB is equal to the sulfate present.

3.0 Interferences

3.1 The ion exchange column eliminates interferences from multivalent cations. A mid-scale sulfate standard containing Ca^{++} should be analyzed periodically to insure that the column is functioning properly.

3.2 Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion exchange resin.

3.3 Turbid samples should be filtered or centrifuged.

4.0 Apparatus

4.1 Technicon AutoAnalyzer consisting of:

4.1.1 Sampler I.

4.1.2 Manifold-high or low level (Figure I).

4.1.3 Proportioning pump.

4.1.4 Colorimeter equipped with 15 mm flow cell and 460 nm interference filters.

4.1.5 Recorder.

4.1.6 Digital Printer for AAII (optional).

5.0 Reagents

5.1 Barium chloride: Dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 ml of distilled water and dilute to 1 liter.

5.2 Methylthymol blue: Dissolve 0.1182 g of methylthymol blue (3'3"-Bis-N,N-bis carboxymethyl-amino methylthymolsulfone-phthalein pentasodium salt) in 25 ml of barium chloride solution (5.1). Add 4 ml of 1.0 N hydrochloric acid which changes the color to bright orange. Add 71 ml of water and dilute to 500 ml with ethanol. The pH of this solution is 2.6. This reagent should be prepared the day before and stored in a brown plastic bottle in the freezer.

5.3 Buffer, pH 10.5 ± 0.5: Dissolve 6.75 g of ammonium chloride in 500 ml of distilled water. Add 57 ml of concentrated ammonium hydroxide and dilute to one liter with distilled water.

5.4 Buffered EDTA: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer (5.3), and dilute to one liter with buffer.

5.5 Sodium hydroxide solution, (50%): Dissolve 500 g NaOH in 600 ml of distilled water, cool, and dilute to 1 liter.

5.6 Sodium hydroxide, 0.18N: Dilute 14.4 ml of sodium hydroxide solution (5.5) to 1 liter.

5.7 Ion exchange resin: Bio-Rex 70, 20-50 mesh, sodium form, Bio-Rad Laboratories, Richmond, California. Free from fines by stirring with several portions of deionized water and decant the supernate before settling is complete.

5.8 Dilution Water: Add 0.75 ml of sulfate stock solution (5.9) and 3 drops of Brij-35 to 2 liters of distilled water.

5.9 Sulfate stock solution, 1 ml = 1 mg SO_4: Dissolve 1.479 g of dried (105°C) Na_2SO_4 in distilled water and dilute to 1 liter.

5.10 Dilute sulfate solution, 1 ml = 0.1 mg SO_4: Dilute 100 ml of sulfate stock solution (5.9) to 1 liter.

5.11 High level working standards, 10-300 mg/l: Prepare high level working standards by diluting the following volumes of stock standard (5.9) to 100 ml.

ml of Stock Solution	Conc., mg/l
1	10
5	50
10	100
15	150
25	250
30	300

5.12 Low level working standards, 1-30 mg/liter: Prepare low level working standards by diluting the following volumes of dilute sulfate solution (5.10) to 100 ml.

ml of Stock Solution	Conc., mg/l
0.5	0.05
1	1.0
5	5.0
10	10.0
15	15.0
25	25.0
30	30.0

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Refrigerate at 4° C.

7.0 Procedures

7.1 Set up manifold for high (10-300 mg SO_4/liter) or low (0.5-30 mg SO_4/liter) level samples as described in Figure I.

7.2 The ion exchange column is prepared by pulling a slurry of the resin into a piece of glass tubing 7.5 inches long, 2.0 mm I.D. and 3.6 mm O.D. This is conveniently done by using a pipet and a loose fitting glass wool plug in the tubing. Care should be taken to avoid allowing air bubbles to enter the column. If air bubbles become trapped, the column should be prepared over again. The column can exchange the equivalent of 35 mg of calcium. For the high level manifold this corresponds to about 900 samples with 200 mg/liter Ca. The column should be prepared as often as necessary to assure that no more than 50% of its capacity is used up.

7.3 Allow the colorimeter, recorder and printer to warm up for 30 minutes. Pump all reagents until a stable baseline is achieved.

7.4 Analyze all working standards in duplicate at the beginning of a run to develop a standard curve. The A and B control standards are analyzed every hour to assure that the system remains properly calibrated. Since the chemistry is non-linear the 180 mg/liter standard is set at 50% on the recorder using the standard calibration control on the colorimeter.

7.5 At the end of each day, the system should be washed with the buffered EDTA solution (5.4). This is done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then in the buffered EDTA solution for 10 minutes. Wash the system with water for 15 minutes before shutting down.

7.6 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with the standard curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

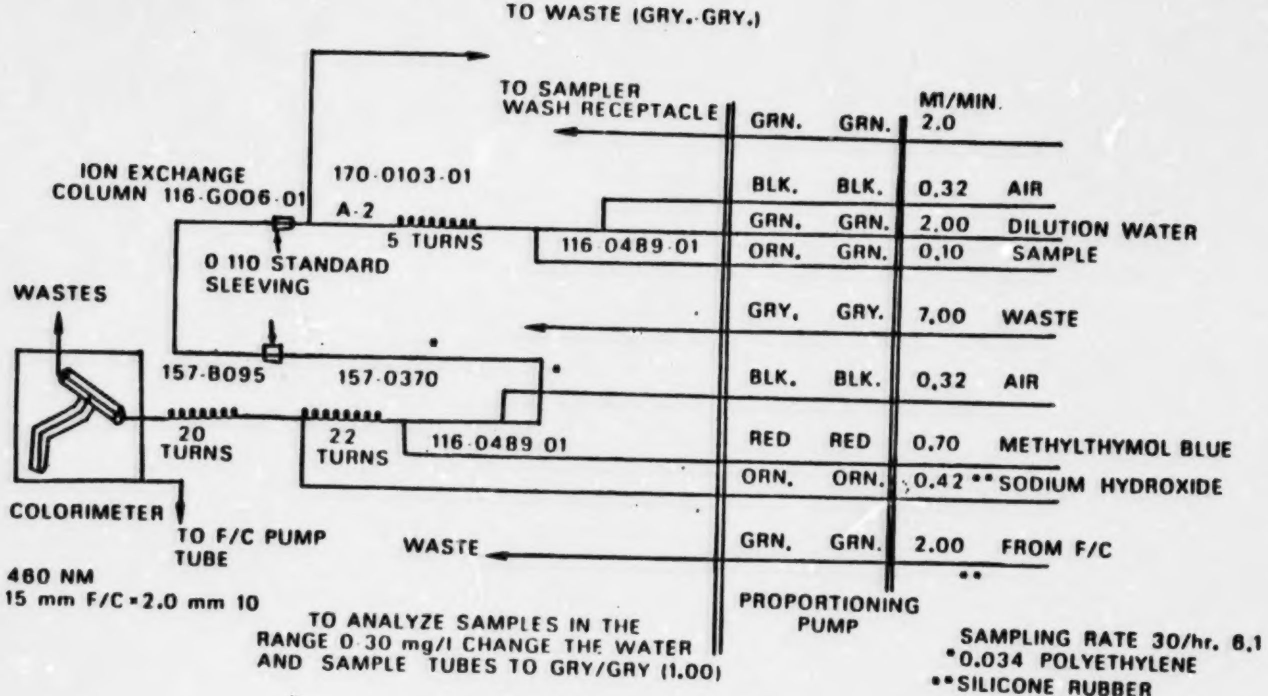

TO WASTE (GRY.-GRY.)
TO SAMPLER WASH RECEPTACLE
ION EXCHANGE COLUMN 116-G006-01
170-0103-01
A-2
5 TURNS
116-0489-01
0 110 STANDARD SLEEVING
WASTES
157-8095
157-0370
20 TURNS
22 TURNS
116-0489 01
COLORIMETER
TO F/C PUMP TUBE
460 NM
15 mm F/C=2.0 mm 10
WASTE
MI/MIN.
GRN. GRN. 2.0
BLK. BLK. 0.32 AIR
GRN. GRN. 2.00 DILUTION WATER
ORN. GRN. 0.10 SAMPLE
GRY. GRY. 7.00 WASTE
BLK. BLK. 0.32 AIR
RED RED 0.70 METHYLTHYMOL BLUE
ORN. ORN. 0.42 ** SODIUM HYDROXIDE
GRN. GRN. 2.00 FROM F/C
**
PROPORTIONING PUMP
TO ANALYZE SAMPLES IN THE RANGE 0-30 mg/l CHANGE THE WATER AND SAMPLE TUBES TO GRY/GRY (1.00)
SAMPLING RATE 30/hr. 6,1
*0.034 POLYETHYLENE
**SILICONE RUBBER

FIGURE 1 SULFATE MANIFOLD AA11

METHOD 9037

SULFATE (GRAVIMETRIC)

1.0 Scope and Application

1.1 This method is applicable to ground, drinking, surface and saline waters, and domestic and industrial wastes.

2.0 Summary of Method

2.1 Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. After a period of digestion, the precipitate is filtered, washed with hot water until free of chloride, ignited, and weighed as $BaSO_4$.

3.0 Interferences

3.1 High results may be obtained for samples that contain suspended matter, nitrate, sulfite and silica.

3.2 Alkali metal sulfates frequently yield low results. This is especially true of alkali hydrogen sulfates. Occlusion of alkali sulfate with barium sulfate causes the substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfate of alkali metal acts similarly and decomposes when heated. Heavy metals such as chromium and iron cause low results by interfering with complete precipitation and by formation of heavy metal sulfates.

4.0 Apparatus

4.1 Steam bath.

4.2 Drying oven, equipped with thermostatic control.

4.3 Muffle furnace with heat indicator.

4.4 Desiccator.

4.5 Analytical balance, capable of weighing to 0.1 mg.

4.6 Filter paper, acid washed, ashless hard-finish filter paper sufficiently retentive for fine precipitates.

5.0 Reagents

5.1 Methyl red indicator solution: Dissolve 100 mg methyl red sodium salt in distilled water in a 100-ml volumetric flask and dilute to the mark with distilled water.

5.2 Hydrochloric acid, HCl, 1 + 1.

5.3 Barium chloride solution: Dissolve 100 g $BaCl_2 \cdot 2H_2O$ in 1 liter of distilled water. Filter through a membrane filter or hard-finish filter paper. One ml of this reagent is capable of precipitating approximately 40 mg SO_4.

5.4 Silver nitrate-nitric acid reagent: Dissolve 8.5 g $AgNO_3$ and 0.5 ml conc. HNO_3 in 500 ml distilled water.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Preserve by refrigerating at 4° C.

7.0 Procedure

7.1 Removal of silica: If silica concentration is greater than 25 mg/liter.

7.1.1 Evaporate sample nearly to dryness in a platinum dish on a steam bath.

7.1.2 Add 2 ml HCl solution (5.2), tilt dish, and rotate until acid contacts all of the residue.

7.1.3 Continue evaporation to dryness.

7.1.4 Complete drying in an oven at 180° C.

7.1.5 If organic matter is present, char over a flame.

7.1.6 Moisten with 2 ml distilled water and 1 ml HCl solution (5.2).

7.1.7 Evaporate to dryness on a steam bath.

7.1.8 Add 2 ml HCl solution (5.2).

7.1.9 Take up soluble residue in hot distilled water and filter.

7.1.10 Wash the insoluble silica with several small portions of hot distilled water.

7.1.11 Combine filtrate and washings.

7.2 Precipitation of Barium Sulfate

7.2.1 If necessary, treat clarified sample to remove interfering agents.

7.2 2 Adjust to contain approximately 50 mg SO_4 ion in a 250 ml volume.

7.2 3 Adjust acidity with HCl solution (5.2) to pH 4.5 to 5.0 using pH meter or orange color of methyl red indicator (5.1).

7.2.4 Add an additional 1 to 2 ml HCl soltuion (5.2).

7.2 5 For lower concentrations of sulfate ion fix the total volume at 150 ml.

7.2 6 Heat to boiling and, while stirring gently, add warm $BaCl_2$ solution (5.3) slowly, until precipitation appears to be complete; then add approximately 2 ml in excess.

7.2 7 If amount of precipitate is small, add a total of 5 ml $BaCl_2$ solution (5.3).

7.2 8 Digest the precipitate at 80 to 90° C preferably overnight but for not less than 2 hours.

7.3 Filtration and Weighing

7.3.1 Mix a little ashless filter paper pulp with the $BaSO_4$ and filter at room temperature.

7.3.2 Wash the precipitate with small portions of warm distilled water until the washings are free of chloride as indicated by testing with silver nitrate-nitric acid reagent (5.4).

7.3.3 Dry the filter and precipitate.

7.3.4 Ignite at 800° C for 1 hour. DO NOT LET THE FILTER PAPER FLAME.

7.3.5 Cool in a desiccator and weigh.

7.4 Calculation

$$\text{mg/liter } SO_4 = \frac{\text{mg } BaSO_4 \times 411.5}{\text{ml sample}}$$

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 Precision and Accuracy

9.1 A synthetic unknown sample containg 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 250 µg/l nitrite N, 1.1 mg/l nitrate N and 42.5 mg/l alkalinity (contributed by $NaHCO_3$), was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.

METHOD 9038

SULFATE (TURBIDIMETRIC)

1.0 Scope and Application

1.1 This method is applicable to ground, drinking and surface waters, and domestic and industrial wastes.

1.2 This method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/liter.

1.3 The minimum detectable limit is approximately 1 mg/liter sulfate.

2.0 Summary of Method

2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer, or spectrophotometer and compared to a curve prepared from standard sulfate solution.

2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.

2.3 Silica in concentrations over 500 mg/liter will interfere.

3.0 Interferences

3.1 Color and turbidity due to the sample matrix can cause positive interferences which must be accounted for by use of blanks.

4.0 Apparatus

4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.

4.2 Photometer: one of the following which are given in order of preference.

4.2.1 Nephelometer.

4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.

4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.

4.3 Stopwatch if the magnetic stirrer is not equipped with an accurate timer.

4.4 Measuring spoon, capacity 0.2 to 0.3 ml.

5.0 Reagents

5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g $NaCl$ in solution in a container. Add 50 ml glycerol and mix.

5.2 Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh.

5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250° C for 4 hours and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-liter volumetric flask and fill to the mark with distilled water.

5.4 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.

5.5 Standard sulfate solution (1.00 ml = 100 µg SO_4): Prepare by either 5.5.1 or 5.5.2.

5.5.1 Standard sulfate solution from H_2SO_4

5.5.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3 to 5 min. under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.5.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.5.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization *versus* 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.5.1.3 Place 10 ml standard sulfuric acid, 0.02 N (5.5.1.2) in a 100-ml volumetric flask and dilute to the mark.

5.5.2 Standard sulfate solution from Na_2SO_4: Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Preserve by refrigerating at 4° C.

7.0 Procedure

7.1 Formation of barium sulfate turbidity.

7.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a a 250 Erlenmeyer flask.

7.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

7.1.3 Mix in the stirring apparatus.

7.1.4 While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals (5.2) and begin timing immediately.

7.1.5 Stir exactly 1.0 minutes at constant speed.

7.2 Measurement of barium sulfate turbidity.

7.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

7.2.2 Measure turbidity at 30-second intervals for 4 minutes.

7.2.3 Record the maximum reading obtained in the 4-minute period.

7.3 Preparation of calibration curve.

7.3.1 Prepare calibration curve using standard sulfate solution (5.5).

7.3.2 Space standards at 5 mg/liter increments in the 0-40 mg/liter sulfate range.

7.3.3 Above 50 mg/liter the accuracy decreases and the suspensions lose stability.

7.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.

7.4 Correction for sample color and turbidity.

7.4.1 Run a sample blank using the procedure 7.1 and 7.2 without the addition of barium chloride (7.1.4).

7.5 Calculations.

7.5.1 Read mg SO_4 from calibration curve.

$$\text{mg } SO_4/\text{liter} = \frac{\text{mg } SO_4 \times 1{,}000}{\text{ml sample}}$$

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 Precision and Accuracy

9.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviaton mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses.)

9.2 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 0.250 mg/l nitrite N, 1.1 mg/l nitrate N, and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

METHOD 9060

TOTAL ORGANIC CARBON

1.0 Scope and Application

1.1 Method 9060 is used to determine the concentration of organic carbon in groundwater, surface, and saline waters, domestic and industrial wastes. Exclusions are noted in Sections 2 and 3. Method 9060 is most applicable to measurement of organic carbon above 1 mg/l.

2.0 Summary of Method

2.1 Organic carbon is measured using a carbonaceous analyzer. These instruments convert the organic carbon in a sample to carbon dioxide (CO_2) by either catalytic combustion or wet chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured. The forms of carbon that can be measured by Method 9060 are:

(1) soluble, nonvolatile organic carbon; for instance, natural sugars

(2) soluble, volatile organic carbon; for instance, mercaptans

(3) insoluble, partially volatile carbon; for instance, oils

(4) insoluble, particulate carbonaceous materials; for instance, cellulose fibers

(5) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles

2.3 The carbon measurement is used to assess the potential oxygen-demanding load of organic material on a receiving stream. Carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis.

3.0 Interferences

3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipet. The openings of the syringe or pipet limit the maximum size of particles which may be included in the sample.

4.0 Apparatus and Materials

4.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

4.2 Apparatus for total and dissolved organic carbon

4.2.1 Several companies manufacture analyzers for measuring carbonaceous material in liquid samples. The most appropriate system should be selected based on considerations of the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

4.2.2 No specific analyzer is recommended as superior.

5.0 Reagents

5.1 Distilled water used in preparation of standards and for dilution of samples should be ultrapure to reduce the carbon concentration of the blank. Carbon-dioxide-free, double-distilled water is recommended. Ion-exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

5.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml. NOTE: Sodium oxalate and acetic acid are not recommended as stock solutions.

5.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

5.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100-ml volumetric flask. Dissolve with distilled water.

5.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 5.3. NOTE: This standard is not required by some instruments.

5.6 Blank solution: Use the same distilled water (or similar quality water) as was used to prepare the standard solutions.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. NOTE: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, 1-qt cubitainers did not show any increase in organic carbon after 2 weeks exposure.

6.3 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples should be kept cool (4° C) and protected from sunlight and atmospheric oxygen.

6.4 In instances where analysis cannot be performed within 2 hr from time of sampling, the sample is acidified (pH less than or equal to 2) with HCl or H_2SO_4.

7.0 Procedure

7.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

7.2 For calibration of the instrument, a series of standards that encompass the expected concentration range of the samples should be used.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

METHOD 9065

PHENOLICS (SPECTROPHOTOMETRIC, MANUAL 4-AAP WITH DISTILLATION)

1.0 Scope and Application

1.1 This method is applicable to the analysis of ground, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials at the 5 µg/liter level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

1.3 The method is capable of measuring phenolic materials that contain more than 50 µg/liter in the aqueous phase (without solvent extraction) using phenol as a standard.

1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2.0 Summary of Method

2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.

3.0 Interferences

3.1 For most samples a preliminary distillation is required to remove interfering materials.

3.2 Color response of phenolic materials with 4-amino antipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

3.3 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.

3.4 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

4.0 Apparatus

4.1 Distillation apparatus, all glass consisting of a 1-liter pyrex distilling apparatus with Graham condenser.

4.2 pH meter.

4.3 Spectrophotometer, for use at 460 or 510 nm.

4.4 Funnels.

4.5 Filter paper.

4.6 Membrane filters.

4.7 Separatory funnels, 500 or 1,000 ml.

4.8 Nessler tubes, short or long form.

5.0 Reagents

5.1 Phosphoric acid solution, 1 + 9: Dilute 10 ml of 85% H_3PO_4 to 100 ml with distilled water.

5.2 Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

5.3 Buffer solution: Dissolve 16.9 g NH_4Cl in 143 ml conc. NH_4OH and dilute to 250 ml with distilled water. Two ml should adjust 100 ml of distillate to pH 10.

5.4 Aminoantipyrine solution: Dissolve 2 g of 4AAP in distilled water and dilute to 100 ml.

5.5 Potassium ferricyanide solution: Dissolve 8 g of $K_3Fe(CN)_6$ in distilled water and dilute to 100 ml.

5.6 Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled distilled water and dilute to 1 liter. 1 ml = 1 mg phenol.

5.7 Working solution A: Dilute 10 ml stock phenol solution to 1 liter with distilled water. 1 ml = 10 μg phenol.

5.8 Working solution B: Dilute 100 ml of working solution A to 1000 ml with distilled water. 1 ml = 1 [g phenol.

5.9 Chloroform.

5.10 Ferrous ammomium sulphate.

6.0 Sample Handling and Preservation

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Biological degradation is inhibited by the addition of 1 g/liter of copper sulfate to the sample and add 1 ml H_2SO_4/l. Store at 4° C. The sample should be stable for 28 days.

7.0 Procedure

7.1 Distillation.

7.1.1 Measure 500 ml sample into a beaker. Lower the pH to approximately 4 with 1 + 9 H_3PO_4 (5.1), add 5 ml $CuSO_4$ solution (5.2), and transfer to the distillation apparatus. Omit adding H_2PO_4 and $CuSO_4$ if sample was preserved as described in 6.2.

7.1.2 Distill 450 ml of sample, stop the distillation, and when boiling ceases add 50 ml of warm distilled water to the flask and resume distillation until 500 ml have been collected.

7.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

7.2 Direct photometric method.

7.2.1 Using working solution A (5.7), prepare the following standards in 100 ml volumetric flasks.

ml of working solution A	Conc. [g/liter
0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0
8.0	800.0
10.0	1000.0

7.2.2 To 100 ml of distillate or an aliquot diluted to 100 ml and/or standards, add 2 ml of buffer solution (5.3) and mix. The pH of the sample and standards should be 10 ± 0.2.

7.2.3 Add 2.0 ml aminoantipyrine solution (5.4) and mix.

7.2.4 Add 2.0 ml potassium ferricyanide solution (5.5) and mix.

7.2.5 After 15 minutes read absorbance at 510 nm.

7.3 Chloroform extraction method.

7.3.1 Using working solution B (5.8), prepare the following standards. Standards may be prepared by pipetting the required volumes into the separatory funnels and diluting to 500 ml with distilled water.

ml of working solution B	Conc. µg/liter
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

7.3.2 Place 500 ml of distillate or an aliquot diluted to 500 ml in a separatory funnel. The sample should not contain more than 25 [g phenol.

7.3.3 To sample and standards add 10 ml of buffer solution (5.3) and mix. The pH should be 10 ± 0.2.

7.3.4 Add 3.0 ml aminoantipyrine solution (5.4) and mix.

7.3.5 Add 3.0 ml potassium ferricyanide solution (5.5) and mix.

7.3.6 After three minutes, extract with 25 ml of chloroform (5.9). Shake the separatory funnel at least 10 times, let $CHCl_3$ settle, shake again 10 times and let chloroform settle again.

7.3.7 Filter chloroform extracts through filter paper. Do not add more chloroform.

7.3.8 Read the absorbance of the samples and standards against the blank at 460 nm.

CAUTION: This method should be performed in a hood since chloroform is toxic.

7.4 Calculation.

7.4.1 Prepare a standard curve by plotting the absorbance value of standards versus the corresponding phenol concentrations.

7.4.2 Obtain concentration value of sample directly from standard curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 3.8, 15, 43 and 89 µg/l, the standard deviations were ±0.5, ±0.6, ±0.6 and ±1.0 µg/l, respectively. At concentrations of 73, 146, 299 and 447 µg/l, the standard deviations were ±1.0, ±1.8, ±4.2 and ±5.3 µg/l, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 5.3 and 82 µg/l, the recoveries were 78% and 98%. At concentrations of 168 and 489 µg/l, the recoveries were 97% and 98%, respectively.

METHOD 9066

PHENOLICS (COLORIMETRIC, AUTOMATED 4-AAP WITH DISTILLATION)

1.0 Scope and Application

1.1 This method is applicable to the analysis of ground, drinking, surface and saline waters.

1.2 The method is capable of measuring phenolic materials from 2 to 500 µg/liter in the aqueous phase using phenol as a standard.

2.0 Summary of Method

2.1 This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured at 505 or 520 nm. The same manifold is used with the AAI or AAII.

3.0 Interferences

3.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.

3.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (5.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

3.3 Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptable by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.

4.0 Apparatus

4.1 Technicon Auto Analyzer (I or II).

4.1.1 Sampler equipped with continuous mixer.

4.1.2 Manifold.

4.1.3 Proportioning pump II or III.

4.1.4 Heating bath with distillation coil.

4.1.5 Distillation head.

4.1.6 Colorimeter equipped with a 50-mm flow cell and 505 or 520 nm filter.

4.1.7 Recorder.

5.0 Reagents

5.1 Distillation reagent: Add 100 ml of conc. phosphoric acid (85% H_3PO_4) into 800 ml of distilled water, cool and dilute to 1 liter.

5.2 Buffered potassium ferricyanide: Dissolve 2.0 g potassium ferricyanide, 3.1 g boric acid, and 3.75 g potassium chloride in 800 ml of distilled water. Adjust to pH of 10.3 with 1 N sodium hydroxide (5.3) and dilute to 1 liter. Add 0.5 ml of Brij-35. Prepare fresh weekly.

5.3 Sodium hydroxide (1 N): Dissolve 40 g NaOH in 500 ml of distilled water, cool and dilute to 1 liter.

5.4 4-Aminoantipyrine: Dissolve 0.65 g of 4-aminoantipyrine in 800 ml of distilled water and dilute to 1 liter. Prepare fresh each day.

5.5 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 ml distilled water containing 1 ml H_2SO_4 and dilute to 1 liter with freshly boiled and cooled distilled water.

5.6 Stock phenol: Dissolve 1.00 g phenol in 500 ml of distilled water and dilute to 1000 ml. Add 1 g $CuSO_4$ and 0.5 ml conc. H_3PO_4 as preservative. 1.0 ml = 1.0 mg phenol.

5.7 Standard phenol solution A: Dilute 10.0 ml of stock phenol solution (5.6) to 1000 ml. 1.0 ml = 0.01 mg phenol.

5.8 Standard phenol solution B: Dilute 100.0 ml of standard phenol solution A (5.7) to 1000 ml with distilled water. 1.0 ml = 0.001 mg phenol.

5.9 Standard solution C: Dilute 100.0 ml of standard phenol solution B (5.8) to 1000 ml with distilled water. 1.0 ml = 0.0001 mg phenol.

5.10 Using standard solution A,B, or C, prepare the following standards in 100 ml volumetric flasks. Each standard should be preserved by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100.0 ml.

ml of Standard Solution	Conc. µg/liter
Solution C	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
Solution B	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
Solution A	
2.0	200
3.0	300
5.0	500

6.0 Sample Handling and Preservation

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Biological degradation is inhibited by the addition of 1 g/liter of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 4° C and analyzed within 24 hours after collection.

7.0 Procedure

7.1 Set up the manifold as shown in Figures 1 or 2.

7.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

7.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hours may be required to obtain a stable baseline. This two-hour time period may be necessary to remove the residual phenol from the tubing.

7.4 Place appropriate phenol standards in sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples, using glass tubes. If samples have not been preserved as instructed in (6.2), add 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100 ml of sample.

7.5 Switch sample from distilled water to sampler and begin analysis.

7.6 Calculation.

7.6.1 Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentration of samples by comparing sample peak heights with standards.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 3.8, 15, 43 and 89 μg/l, the standard deviations were ±0.5, ±0.6, ±0.6 and ±1.0 μg/l, respectively. At concentrations of 73, 146, 299 and 447 μg/l, the standard deviations were ±1.0, ±1.8, ±4.2 and ±5.3 μg/l, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 5.3 and 82 μg/l, the recoveries were 78% and 98%. At concentrations of 168 and 489 μg/l, the recoveries were 97% and 98%, respectively.

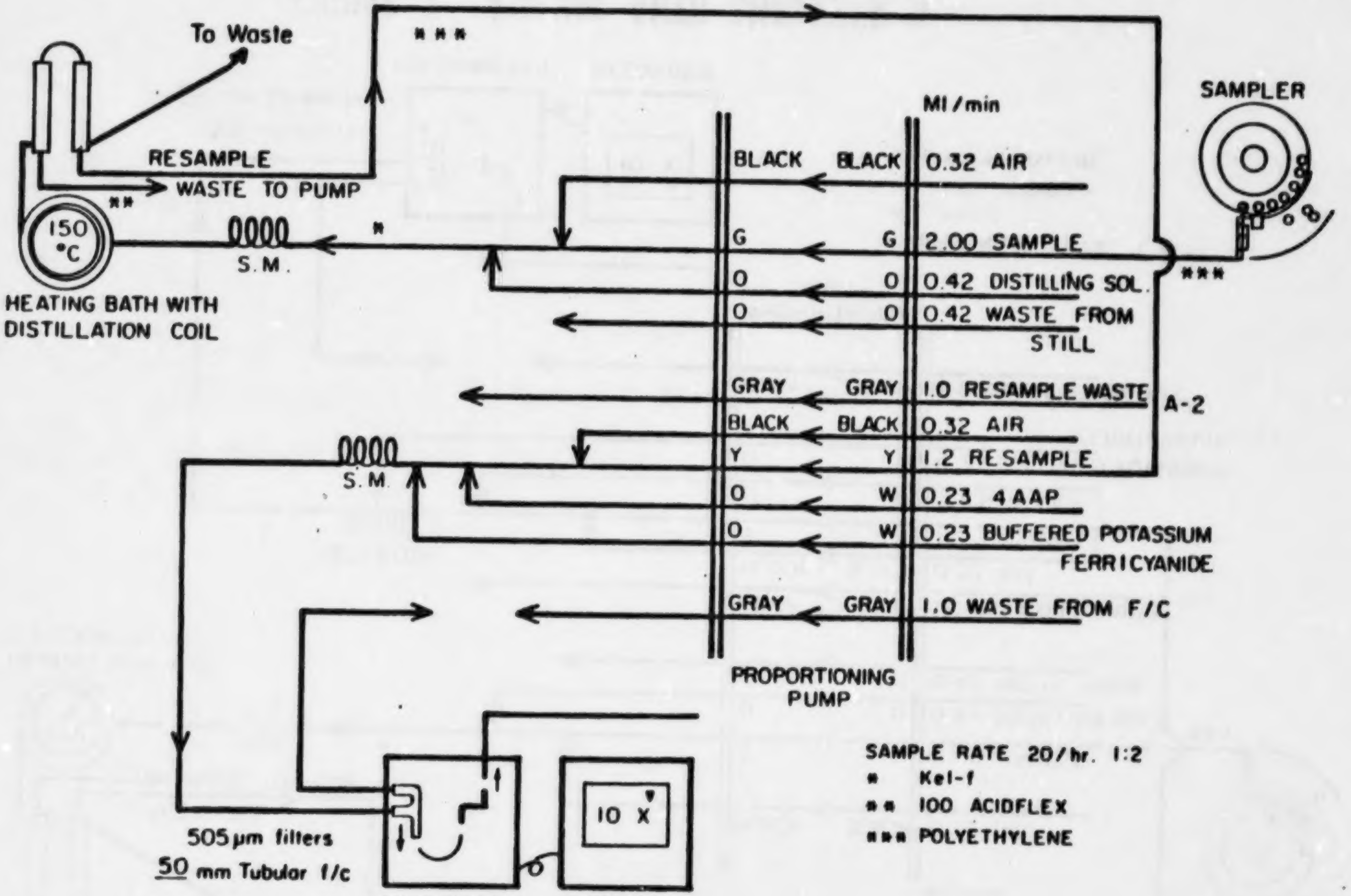

To Waste
RESAMPLE
WASTE TO PUMP
**
150 °C
HEATING BATH WITH DISTILLATION COIL
S.M.
*
***
SAMPLER
***
Ml/min
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
PROPORTIONING PUMP
S.M.
505 μm filters
50 mm Tubular f/c
10 X
COLORIMETER
RECORDER
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE

FIGURE 1. PHENOL AUTO ANALYZER I

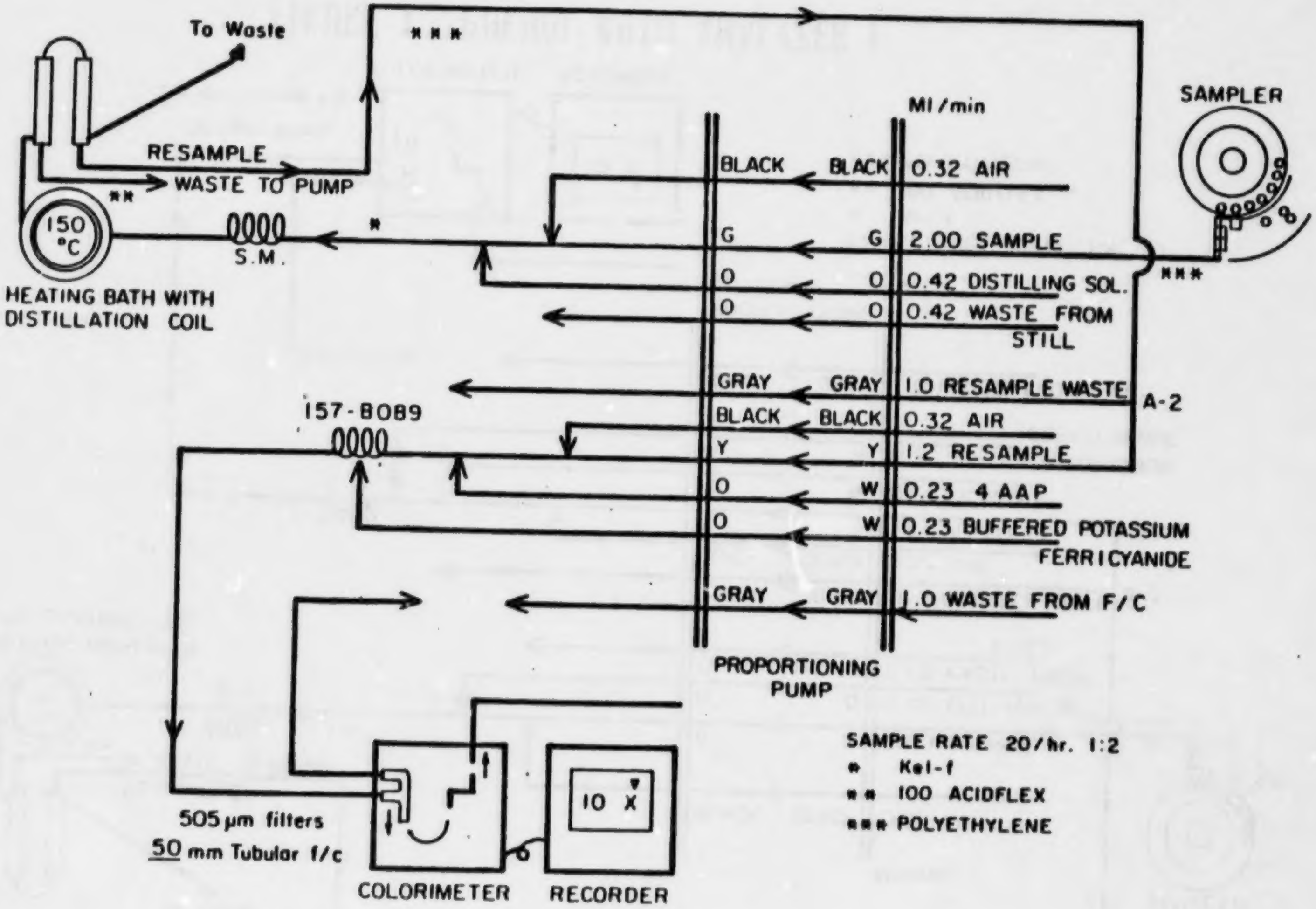

To Waste
* * *
RESAMPLE
WASTE TO PUMP
**
*
150 °C
S.M.
HEATING BATH WITH
DISTILLATION COIL
Ml/min
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
157-B089
SAMPLER
* * *
PROPORTIONING PUMP
505 μm filters
50 mm Tubular f/c
COLORIMETER
RECORDER
10 X
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE

FIGURE 2. PHENOL AUTO ANALYZER II

METHOD 9067

PHENOLICS (SPECTROPHOTOMETRIC, MBTH WITH DISTILLATION)

1.0 Scope and Application

1.1 This method is applicable to the analysis of ground, drinking, surface and saline waters, and domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials at the 2 ug/liter level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

1.3 The method is capable of measuring phenolic materials that contain from 50 to 1000 ug/l in the aqueous phase (without solvent extraction) using different kinds of phenols.

1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2.0 Summary of Method

2.1 This method is based on the coupling of phenol with MBTH in an acid medium using ceric ammonium sulfate as an oxidant. The coupling takes place in the p-position; if this position is occupied, the MBTH reagent will react at a free o-position. The colors obtained have maximum absorbance from 460-595 nm. For phenol and most phenolic mixtures, the absorbance is 520 and 490 nm.

3.0 Interferences

3.1 For most samples a preliminary distillation is required to remove interfering materials.

3.2 Color response of phenolic materials with MBTH is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason, phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

3.3 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_2SO_4 and aerating briefly by stirring and adding $CuSO_4$.

3.4 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (5.11). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

3.5 Phosphate causes a precipitate to form; therefore, phosphoric acid should not be used for preservation. All glassware should be phosphate free.

3.6 High concentrations of aldehydes may cause interferences.

4.0 Apparatus

4.1 Distillation apparatus: All glass consisting of a 1-liter pyrex distilling apparatus with Graham condensor.

4.2 pH meter.

4.3 Spectrophotometer.

4.4 Funnels.

4.5 Filter paper.

4.6 Membrane filters.

4.7 Separatory funnels.

5.0 Reagents

5.1 Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5\ H_2O$ in distilled water and dilute to 1 liter.

5.2 Sulfuric acid, 1 N: Add 28 ml of conc. H_2SO_4 to 900 ml of distilled water, mix and dilute to 1 liter.

5.3 MBTH solution, 0.05%: Dissolve 0.1 g of 3-methyl-2-benzothiazolinone hydrazone hydrochloride in 200 ml of distilled water.

5.4 Ceric ammonium sulfate solution: Add 2.0 g of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ and 2.0 ml of conc. H_2SO_4 to 150 ml of distilled water. After the solid has dissolved dilute to 200 ml with distilled water.

5.5 Buffer solution: Dissolve in the following order, 8 g of sodium hydroxide, 2 g EDTA (disodium salt), and 8 g boric acid in 200 ml of distilled water. Dilute to 250 ml with distilled water.

5.6 Working buffer solution: Make a working solution by mixing an appropriate volume of buffer solution (5.5) with an equal volume of ethanol.

5.7 Chloroform.

5.8 Stock phenol: Dissolve 1.00 g phenol in 500 ml of distilled water and dilute to 1000 ml. Add 1 g $CuSO_4$ and 0.5 ml conc. H_2SO_4 as preservative. 1.0 ml = 1.0 mg phenol.

5.9 Standard phenol solution A: Dilute 10.0 ml of stock phenol solution (5.8) to 1000 ml. 1.0 ml = 0.01 mg phenol.

5.10 Standard phenol solution B: Dilute 100.0 ml of standard phenol solution A (5.9) to 1000 ml with distilled water. 1.0 ml = 0.001 mg phenol.

5.11 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 ml distilled water containing 1 ml concentration H_2SO_4 and dilute to one liter with freshly sorted and cooled distilled water.

6.0 Sample Handling and Preservation

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Biological degradation is inhibited by the addition of 1 g/liter of copper sulfate to the sample and acidification to a pH of less than 4 with sulfuric acid. The sample should be kept at 4° C and analyzed within 24 hours after collection.

7.0 Procedure

7.1 Distillation.

7.1.1 To 500 ml of sample add 5 ml of copper sulfate solution (5.1) and adjust the pH to approximately 4 with 1 N sulfuric acid solution (5.2).

7.1.2 Distill over 450 ml of sample, add 50 ml of warm distilled water to flask, and resume distillation until 500 ml has been collected.

7.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

7.2 Concentration above 50 µg/l.

7.2.1 To 100 ml of distillate or an aliquot diluted to 100 ml, add 4 ml of MBTH solution (5.3).

7.2.2 After 5 minutes, add 2.5 ml of ceric ammonium sulfate solution (5.4).

7.2.3 Wait another 5 minutes and add 7 ml of working buffer solution (5.6).

7.2.4 After 15 minutes, read the absorbance at 520 nm against a reagent blank. The color is stable for 4 hours.

7.3 Concentration below 50 µg/l.

7.3.1 To 500 ml of distillate in a separatory funnel, add 4 ml of MBTH solution (5.3).

7.3.2 After 5 minutes, add 2.5 ml of ceric ammonia sulfate solution (5.4).

7.3.3 After an additional 5 minutes, add 7 ml of working buffer solution (5.6).

7.3.4 After 15 minutes, add 25 ml of chloroform. Shake the separatory funnel at least 20 times. Allow the layer to separate, and pass the chloroform layer through filter paper.

7.3.5 Read the absorbance at 490 nm against a reagent blank.

7.4 Calculation.

7.4.1 Prepare a standard curve by plotting absorbance against concentration values.

7.4.2 Obtain concentration value of sample directly from prepared standard curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

METHOD 9070

OIL AND GREASE, TOTAL, RECOVERABLE

(Gravimetric, Separatory Funnel Extraction)

1.0 Scope and Application

1.1 This method includes the measurment of fluorocarbon-113 extractable matter from surface and saline waters, industrial, domestic and aqueous solid wastes. It is applicable to the determination of relatively nonvolatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.

1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation.

1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

1.4 The method covers the range from 5 to 1000 mg/l of extractable material.

2.0 Summary of Method

2.1 The 1 liter sample is acidified to a low pH (2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue is weighed.

3.0 Interferences

3.1 Matrix interferences will likely be coextracted from the sample. The extent of these interferences will vary from waste to waste depending on the nature and diversity of the waste being analyzed. A procedural blank should be used for the compounds of interest prior to the use of this method.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 Apparatus

4.1 Separatory funnel, 2,000 ml, with Teflon stopcock.

4.2 Vacuum pump, or other source of vacuum.

4.3 Flask, boiling, 125 ml (Corning No. 4100 or equivalent).

4.4 Distilling head, Claisen or equivalent.

4.5 Filter paper, Whatman No. 40, 11 cm.

5.0 Reagents

5.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.

5.2 Fluorcarbon-113, (1,1,2-trichloro-1,2,2-trfluoroethane), b. p. 48°C.

5.3 Sodium sulfate, anhydrous crystal.

6.0 Sample Collection, Preservation and Handling

6.1 Collect a representative sample in a wide-mouth glass bottle that has been rinsed with the solvent to remove any detergent film, and acidify in the sample bottle.

6.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

7.0 Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (5.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Tare a boiling flask (pre-dried in an oven at 103°C and stored in a desiccator).

7.4 Add 30 ml fluorocarbon-113 (5.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent moistened filter paper.

Note: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (5.3) into the filter paper cone and slowly draining the emulstion through the salt. Additonal 1 g portions can be added to the cone as required.

7.5 Repeate (7.4) twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10-20 ml solvent and collect the rinsings in the flask.

7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.

7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from heat source and wipe the outside to remove excess moisture and fingerprints.

7.9 Cool the boiling flask in a desiccator for 30 minutes and weight.

8.0 Quality Control

8.1 A representative sample should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (5.1) at the time of collection and refrigerated at 4°C.

8.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

9.0 Calculation

9.1 mg/l total oil and grease = $\frac{R - B}{V}$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.
B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.
V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

10.0 Precision and Accuracy

10.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93 percent with a standard deviation of +0.9 mg/l.

References:

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 515, Method 502A (1975).
2. Blum, K.A., and Taras, M.J., "Determination of Emulsifying Oil in Industrial Wastewater," JWPCF Research Suppl. 40, R404 (1968).

METHOD 9071

EXTRACTION METHOD FOR SLUDGE SAMPLES

1.0 Scope and Application

1.1 Method 9071 is used to recover low levels of oil and grease (10 mg/L) by chemically drying liquid samples and then extracting via the Soxhlet apparatus.

1.2 Method 9071 is used when relatively polar, heavy petroleum fractions are present, or when the levels of nonvolatile greases challenge the solubility limit of the solvent.

1.3 Specifically, Method 9071 is suitable for biological lipids, mineral hydrocarbons and some industrial wastewaters.

1.4 Method 9071 is not recommended for measurement of low-boiling fractions thaat volatilize at temperatures below 70 C.

2.0 Summary Method

2.1 A 20 g sample of wet sludge with a known dry-solids content is acidified to pH 2.0 with 0.3 ml conc HCl.

2.2 Magnesium sulfate monohydrate will combine with 75 percent of its own weight in water in forming Mg $SO_4.7H_2O$ and is used to dry the acidified sludge sample.

2.3 After drying, the oil and grease are extracted with trichlorotrifluoroethane using the Soxhlet apparatus.

3.0 Interferences

3.1 The method is entirely empirical and duplicate results can be obtained only by strict adherence to all details of the processes.

3.2 The rate and time of extraction in the Soxhlet apparatus must be exactly as directed because of varying solubilities of the different greases.

3.3 The length of time required for drying and cooling extracted material must be constant.

3.4 A gradual increase in weight may result due to the absorption of oxygen; a gradual loss of weight may result due to volatilization.

4.0 Apparatus and Materials

4.1 Extraction apparatus, Soxhlet

4.2 Analytical balance

4.3 Vacuum pump or some other vacuum source

4.4 Extraction thimble, filter paper

4.5 Glass wool or small glass beads to fill thimble

4.6 Grease-free cotton. Extract nonabsorbent cotton with solvent

4.7 Beaker 150 ml

4.8 pH indicator to determine acidity

4.9 Porcelain mortar

4.10 Extraction flask, 150 ml

4.11 Distilling apparatus, water bath at 70 C

4.12 Desiccator

5.0 Reagents

5.1 Hydrochloric acid, HCl conc.

5.2 Magnesium sulfate monohydrate: Prepare $MgSO_4.H_2O$ by overnight of a thin layer in an oven at 150 C.

5.3 Trichlorotrifluoroethane (1,1,2-trichloro-1,2,2-trifluoroethane), boiling point 47 C. The solvent should leave no measureable residue on evaporation; distill if necessary.

6.0 Sample Collection, Preservation and Handling

6.1 Transfers of the solvent trichlorotrifluoroethane should not involve any plastic tubing in the assembly.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. Liquids may be transferred using a glass hypodermic syringe. Solids may be transferred using a spatula, spoon or coring device.

6.3 Any turbidity or suspended solids in the extraction flask should be removed by filtering through grease-free cotton.

7.0 Procedure

7.1 Weight out a 20 ± 0.5g sample of wet sludge with a known dry-solid content. Place in a 150 ml beaker.

7.2 Acidify to pH 2.0 with approximately 0.3 ml conc HCl.

7.3. Add 25 g prepared $MgSO_4.H_2O$ and stir to a smooth paste.

7.4 Spread on sides of beaker to facilitate evaporation. Let stand about 15-30 min. or until substance is solidified.

7.5 Remove solids and grind to a fine powder in a mortar.

7.6 Add the powder to the paper extraction thimble.

7.7 Wipe beaker and mortar with pieces of filter paper moistened with solvent and add to thimble.

7.8 Fill thimble with glass wool (or glass beads).

7.9 Extract in Soxhlet apparatus using trichlorotrifluoroethane at a rate of 20 cycles/hr for four hours.

7.10 Filter out any turbidity in the extraction flask using grease-free cotton.

7.11 Rinse flask and cotton with solvent.

7.12 Connect the boiling glask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for resue. A solvent blank should accompany each set of samples.

7.13 When the temperature in the distilling head reaches 50°C or the flask appears dry, remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.

7.14 Cool the boiling flask in a desiccator for 30 minutes and weigh.

7.15 Calculate oil and grease as a percentage of the total dry solids. Generally:

$$\text{\% of oil and grease} = \frac{\text{gain in weight of flask, g} \times 100}{\text{weight of wet solids, g} \times \text{dry solids fraction}}$$

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank sample should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis.

8.3 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

METHOD 9080[1]

CATION-EXCHANGE CAPACITY (AMMONIUM ACETATE)

1.0 Scope and Application

1.1 Method 9080 is used to determine the cation-exchange capacity of soils. The method is not applicable to the following soil types. Soils containing appreciable amounts of vermiculite clays, kaolin, halloysite, or other 1:1-type clay minerals should be analyzed by the sodium acetate method (Method 9081). This method (9081) is also generally the preferred method for very calcareous soils. For distinctly acid soils, the cation-exchange capacity by summation method (page 900 of reference cited below[1]) should be employed.

2.0 Summary

2.1 The soil is mixed with an excess of 1 N ammonium acetate solution. This results in an exchange of the ammonium cations for exchangeable cations present in the soil. The excess ammonium is removed, and the amount of exchangeable ammonium is determined.

3.0 Interferences

3.1 Soils containing appreciable vermiculite clays, kaolin, halloysite, or other 1:1-type clay minerals will often give lower values for exchange capacity.

3.2 With calcareous soils, the release of calcium carbonate from the soil into the ammonium acetate solution limits the saturation of exchange sites by the ammonium ion. This results in artificially low cation-exchange capacities.

4.0 Apparatus and Materials

4.1 500-ml Erlenmeyer flask.

4.2 55-mm Büchner funnel or equivalent.

4.3 2 mm sieve.

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[1] This method is based on Chapman, H.D., 1965, Cation exchange capacity, pp. 891-900 in C.A. Block (ed.), Method of soil analysis, Part 2: Chemical and microbiological properties (Madison, Wisconsin: Am. Soc. Agron).

4.3 Aeration apparatus (assembled as in Figure 1).

4.3.1 800-ml Kjeldahl flask.

4.3.2 800-ml Erlenmeyer flask.

4.3.3 Glass wool filter.

4.3.4 Glass tubing.

4.3.5 Flow meter.

5.0 Reagents

5.1 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 ml of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 ml of conc. ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 ml. Check the pH of the resulting solution, add more NH_4OH as needed to obtain a reaction of pH 7, and dilute the solution to a volume of 2 liters with water.

5.2 Isopropyl alcohol, 99%.

5.3 Ammonium chloride (NH_4Cl), 1 N, adjusted to pH 7.0 with NH_4OH.

5.4 Ammonium chloride (NH_4Cl), 0.25 N, adjusted to pH 7.0 with NH_4OH.

5.5 Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$), 10%.

5.6 Dilute ammonium hydroxide (NH_4OH): Add 1 volume of conc. NH_4OH to an equal volume of water.

5.7 Silver nitrate ($AgNO_3$), 0.10 N.

5.8 Reagents for aeration option

5.8.1 Sodium carbonate solution (Na_2CO_3), 5%.

5.8.2 Paraffin oil.

5.8.3 Sulfuric acid (H_2SO_4), 0.1 N standard.

5.8.4 Sodium hydroxide (NaOH), 0.1 N standard.

5.8.5 Methyl red indicator, 0.1% in 95% ethyl alcohol.

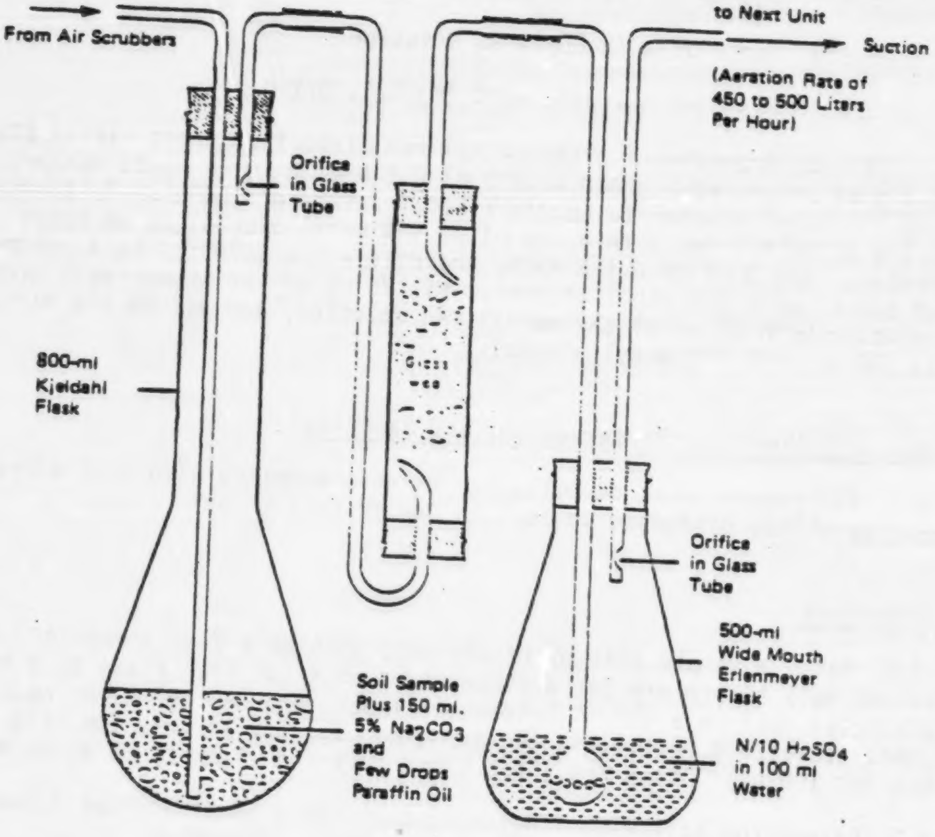
From Air Scrubbers
to Next Unit
Suction
(Aeration Rate of
450 to 500 Liters
Per Hour)
Orifice
in Glass
Tube
Glass
wool
800-ml
Kjeldahl
Flask
Orifice
in Glass
Tube
500-ml
Wide Mouth
Erlenmeyer
Flask
Soil Sample
Plus 150 ml.
5% Na_2CO_3
and
Few Drops
Paraffin Oil
N/10 H_2SO_4
in 100 ml
Water

Figure 1. Diagram of aeration unit for determination of absorbed ammonia. Six to twelve such units is a convenient number for routine work; they can be mounted on a portable rack. (Apparatus as modified by Dr. A. P. Vanselow, Dept. of Soils & Plant Nutrition, Univerity of California, Riverside, Calif.).

5.9 Reagents for distillation option

5.9.1 Sodium chloride, NaCl (acidified): Prepare a 10% aqueous solution of NaCl (ammonium-free), and acidify it with enough HCl to make the solution approximately 0.005 N with respect to acidity.

5.9.2 Sodium hydroxide (NaOH), 1 N.

5.9.3 Boric acid (H_3BO_3), 2% solution.

5.9.4 Standard sulfuric acid (H_2SO_4), 0.1 N.

5.9.5 Bromocresol green-methyl red mixed indicator: Triturate 0.1 g of bromocresol green with 2 ml 0.1 N NaOH in an agate mortar, and add 95% ethyl alcohol to obtain a total volume of 100 ml. Triturate 0.1 g of methyl red with a few ml of 95% ethyl alcohol in an agate mortar. Add 3 ml of 0.1 N NaOH, and dilute the solution to a volume of 100 ml with 95% ethyl alcohol. Mix 75 ml of the bromocresol green solution with 25 ml of the methyl red solution, and dilute the mixture to 200 ml with 95% ethyl alcohol.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

7.0 Procedure

7.1 Seive a sample aliquot of the soil through a 2-mm screen and allow the seived soil to air dry (at a temperature of $\leq$ 60° C). Place 10 g of the air-dried soil in a 500-ml Erlenmeyer flask, and add 250 ml of neutral, 1 N NH_4OAc. (Use 25 g of soil if the exchange capacity is very low, e.g., 3-5 meq per 100 g.) Shake the flask thoroughly and allow it to stand overnight.

7.2 Filter the soil with light suction using a 55-mm Büchner funnel or equivalent. Do not allow the soil to become dry and cracked.

7.3 Leach the soil with the neutral NH_4OAc reagent until no test for calcium can be obtained in the effluent solution. (For the calcium test, add a few drops of 1 N NH_4Cl, 10% ammonium oxalate, and dilute NH_4OH to 10 ml of the leachate in a test tube, and heat the solution to near the boiling point. The presence of calcium is indicated by a white precipitate or turbidity.)

7.4 Then leach the soil four times with neutral 1 N NH_4Cl and once with 0.25 N NH_4Cl.

7.5 Wash out the electrolyte with 150 to 200 ml of 99% isopropyl alcohol. When the test for chloride in the leachate (use 0.10 N $AgNO_3$) becomes negligible, allow the soil to drain thoroughly.

7.6 Determine the adsorbed NH_4, either by the aeration method (Section 7.7) or by the acid-NaCl method (Section 7.8).

7.7 Aeration method

7.7.1 Place an excess of 0.1 N standard H_2SO_4 in a 500-ml Erlenmeyer flask of the aeration apparatus (50 ml is an ample quantity for most soils), and add 10 drops of methyl red indicator and enough distilled water to make the total volume about 100 ml.

7.7.2 Attach the flask to the apparatus. Then transfer the ammonium-saturated sample of soil (from Section 7.5) quantitatively to the 800-ml Kjeldahl flask located in the flow line just before the Erlenmeyer flask with the standard acid. Use a rubber policeman and a stream of distilled water from a wash bottle as needed to complete the transfer.

7.7.3 Add 150 ml Na_2CO_3 solution and a few drops of paraffin oil, and attach the flask to the apparatus.

7.7.4 Apply suction to the outflow end of the apparatus, and adjust the rate of flow to 450 to 500 liters of air per hr. Continue the aeration for 17 hr.

7.7.5 Shut off the suction, and remove the flask. Titrate the residual acid in the absorption solutions with standard 0.1 N NaOH from the original red color through orange to yellow at the end point. From the titration values obtained with the soil and blank solutions, calculate the content of adsorbed ammonium in milligram equivalents per 100 g soil.

7.8 Acid NaCl method

7.8.1 Leach the ammonium-saturated soil from Section 7.5 with 10% acidified NaCl until 225 ml have passed through the sample. Add small portions at a time, allowing each portion to pass through the sample before adding the next portion.

7.8.2 Transfer the leachate quantitatively to an 800-ml Kjeldahl flask, add 25 ml of 1 N NaOH, and distill 60 ml of the solution into 50 ml of 2% H_3BO_3.

7.8.3 Add 10 drops of bromocresol green-methyl red mixed indicator, and titrate the boric acid solution with standard 0.1 N H_2SO_4. The color change is from bluish green through bluish purple to pink at the end point. Run blanks on the reagents. Correct the titration figure for the blanks, and calculate the milliequivalents of ammonium in 100 g of soil.

7.8.4 Results should be reported as "determined with ammonium acetate" at pH 7.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Enjoy a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Material of known cation-exchange capacity must be routinely analyzed.

METHOD 9081[1]

CATION-EXCHANGE CAPACITY (SODIUM ACETATE)

1.0 Scope and Application

1.1 Method 9081 is applicable to most soils, including calcareous and noncalcareous soils. The cation-exchange capacity by summation method (page 900 of reference cited in footnote 1) should be employed for distinctly acid soils.

2.0 Summary of Method

2.1 The soil sample is mixed with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium is then determined by atomic absorption or emission spectroscopy or an equivalent means.

3.0 Interferences

3.1 Interferences can occur during analysis of the extract for sodium content. Thoroughly investigate the chosen analytical method for potential interferences.

4.0 Apparatus and Materials

4.1 50-ml, round-bottom, narrow-neck centrifuge tube and stopper.

4.2 Mechanical shaker.

4.3 100-ml volumetric flask.

5.0 Reagents

5.1 Sodium acetate (NaOAc), 1.0 N: Dissolve 136 g of $NaC_2H_2O_2 \cdot 3H_2O$ in water, and dilute it to 1,000 ml. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the reaction of the solution to pH 8.2.

---

[1] This method is based on Chapman, H.D., 1965, Cation-Exchange Capacity, pp. 891-900 in C.A. Black (ed.), Methods of soil analysis, Part 2: Chemical and microbiological properties (Madison, Wisconsin: Am. Soc. Agron).

5.2 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 ml of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 ml of concentrated ammonium hydroxide (NH_4OH), and add water to obtain a volume of about 1,980 ml. Check the pH of the resulting solution, add more NH_4OH as needed to obtain a reaction of pH 7, and dilute the solution to a volume of 2 liters with water.

5.3 Isopropyl alcohol, 99%.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

7.0 Procedure

7.1 Weigh 4 g of medium- or fine-textured soil or 6 g of coarse-textured soil, and transfer the sample to a 50-ml, round-bottom, narrow-neck centrifuge tube. (A fine soil has > 50% of the particles $\leq$ 0.074 mm, medium soil has > 50% $\geq$ 0.425 mm, while a course soil has more than 50% of its particles $\geq$ 2 mm.

7.2 Add 33 ml of 1.0 N NaOAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

7.3 Decant the liquid, and repeat Section 7.2 three more times.

7.4 Add 33 ml of 99% isopropyl alcohol, stopper the tube, shake it in a mechanical shaker for 5 min and centrifuge it until the supernatant liquid is clear.

7.5 Repeat the procedure described in Section 7.4 two more times.

7.6 Add 33 ml of NH_4OAc solution, stopper the tube, shake it in a mechanical shaker for 5 minutes, and centrifuge it until the supernatant liquid is clear. Decant the washing into a 100-ml volumetric flask.

7.7 Repeat the procedure described in Section 7.6 two more times.

7.8 Dilute the combined washing to the 100-ml mark with ammonium acetate solution and determine the sodium concentration by atomic absorption or emission spectroscopy or an equivalent method.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Materials of known cation-exchange capacity must be routinely analyzed.

METHOD 9090

COMPATIBILITY TEST FOR WASTES AND MEMBRANE LINERS

1.0 Scope and Application

1.1 Method 9090 is intended for use in determining the effects of chemicals in a surface impoundment, waste pile, or landfill on the physical properties of flexible membrane liner materials intended to contain them. Data from these tests will assist in deciding whether a given liner material is acceptable for the intended application.

2.0 Summary of Method

2.1 In order to estimate waste/liner compatibility, the liner material is exposed to the expected chemical environment for periods up to 120 days at room temperature and an elevated temperature. A comparison of the membrane's physical properties before and after these contact periods is used to estimate the properties of the liner when exposed to the waste over time.

3.0 Interferences (Not applicable)

4.0 Apparatus and Materials

4.1 Exposure tanks of a size sufficient to contain the samples with provisions for supporting the specimens so that they do not touch bottom or sides of the tank, or each other, and for stirring the liquid in the tank. The tank shall be equipped with a means of maintaining the solution at temperatures of room temperature and 50±2°C and for preventing evaporation of the solution (e.g., cover equipped with a reflux condenser) with both sides of the liner material exposed to the chemical environment. If the liner has a side which is not exposed to the waste in actual use and which is not designed to withstand exposure to the chemical environment, then such a liner may be treated with only the barrier surface exposed.

4.2 Stress-strain machine suitable for measuring elongation, tensile strength, and tear and puncture resistance.

4.3 Jig for testing puncture resistance for use with FTMS 101B, Method 2065.

4.4 Specimen labels and holders made of materials known to be resistant to the specific wastes.

5.0 Reagents (Not applicable)

6.0 Sample Collection, Preservation, and Handling

6.1 For information on what constitutes a representative sample of the waste fluid, the following guidancedocumetn should be referred to:

> Permit Applicants' Guidance Manual for Hazardous Waste Land Treatment, Storage, and Disposal Facilities; Final Draft; May 1984.

7.0 Procedure

7.1 Obtain a representative sample of the waste fluid.

7.2 Perform the following tests on unexposed samples of the polymeric membrane liner material. Tests for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. See Figure 1 for cutting patterns for nonreinforced liners, and Figure 2 for cutting patterns for reinforces liners.

1. Tear resistance, machine and transferse directions, five specimens each direction for nonreinforced liner materials only.
2. Puncture resistance, five specimens, FTMS 1018, Method 2065.
3. Tensile properties, machine and transverse directions, five tensile specimens in each direction. See Figure 3 for tensile dumbbell cutting pattern dimensions for nonreinforced liner sample.
4. Hardness, Duro A (Duro D if duro A reading is greater than 80), ASTM D2240.
5. Elongation at break. This test is only to be performed on membrane material which does not have a fabric or other nonelastomeric support on its reverse (away from waste) face.

7.3 Cut pieces of the lining material of a size to fit sample holder, and of a sufficient number to permit at least three samples for each waste and each exposure period. Inspect all samples for flaws and discard unsatisfactory ones. Liner materials with fabric reinforcement require close inspection to ensure that threads of the samples are evenly spaced and straight at 90°. Samples containing a fiber scrim support may be floodcoated along the exposed edges with a solution recommended by the liner manufacturer. This solution will typically contain 5-15% solids dissolved in a solvent. The solids content can be the liner formula or the base polymer. Measure the following:

1. Gauge thickness, mil or mm - average of the four corners.
2. Mass, g - to one-hundredth of a gram.
3. Length, cm - average of the lengths of the two sides.
4. Width, cm - average of the widths of the two ends.

TABLE 1. TENSILE AND TEAR TESTING PROTOCOLS

Property to be tested	Type of compound and construction[a]			
	Flexible membrane liners without fabric reinforcement			Fabric-reinforced flexible membrane liners
	XL	TP	CX	FR
Tensile properties				
Method	ASTM D412	ASTM D638	ASTM D638	ASTM D751, Mtd B (modified[b])
Type of specimen	Dumbbell[c]	Dumbbell[c]	Dumbbell[c]	1 in. x 5 in. strip and 2 in. jaw separation
Speed of test	20 ipm	20 ipm	2 ipm	12 ipm
Values to be reported	Tensile strength, psi Elongation at break, % Tensile set after break, % Stress at 100, 200, and 300% elongation, psi	Tensile strength, psi Elongation at break, % Tensile set after break, % Stress at 100, 200, and 300% elongation, psi	Tensile stress at yield, psi Elongation at yield, % Tensile strength at break, psi Elongation at break, % Tensile set after break, % Stress at 100, 200, and 300% elongation, psi	Tensile at fabric break, ppi Elongation at fabric break, % Tensile at ultimate break, ppi Elongation at ultimate break, % Tensile set after break, % Stress at 100, 200, and 300% elongation, ppi
Tear resistance				
Method	ASTM D624	ASTM D1004 (modified[d])	ASTM D1004	(e)
Type of specimen	Die C	Die C[f]	Die C[f]	
Speed of test	20 ipm	20 ipm	2 ipm	

---

[a] XL = Crosslinked or vulcanized; TP = thermoplastic; CX = crystalline; FR = fabric-reinforced (see explanation in Table 2).

[b] Specimen = 1 in. x 5 in. strip; initial jaw separation = 2 in.

[c] See Figure 1.

[d] Crosshead speed = 20 ipm.

[e] No tear resistance is recommended for fabric-reinforced sheetings in the immersion study.

[f] Die C from ASTM D624.

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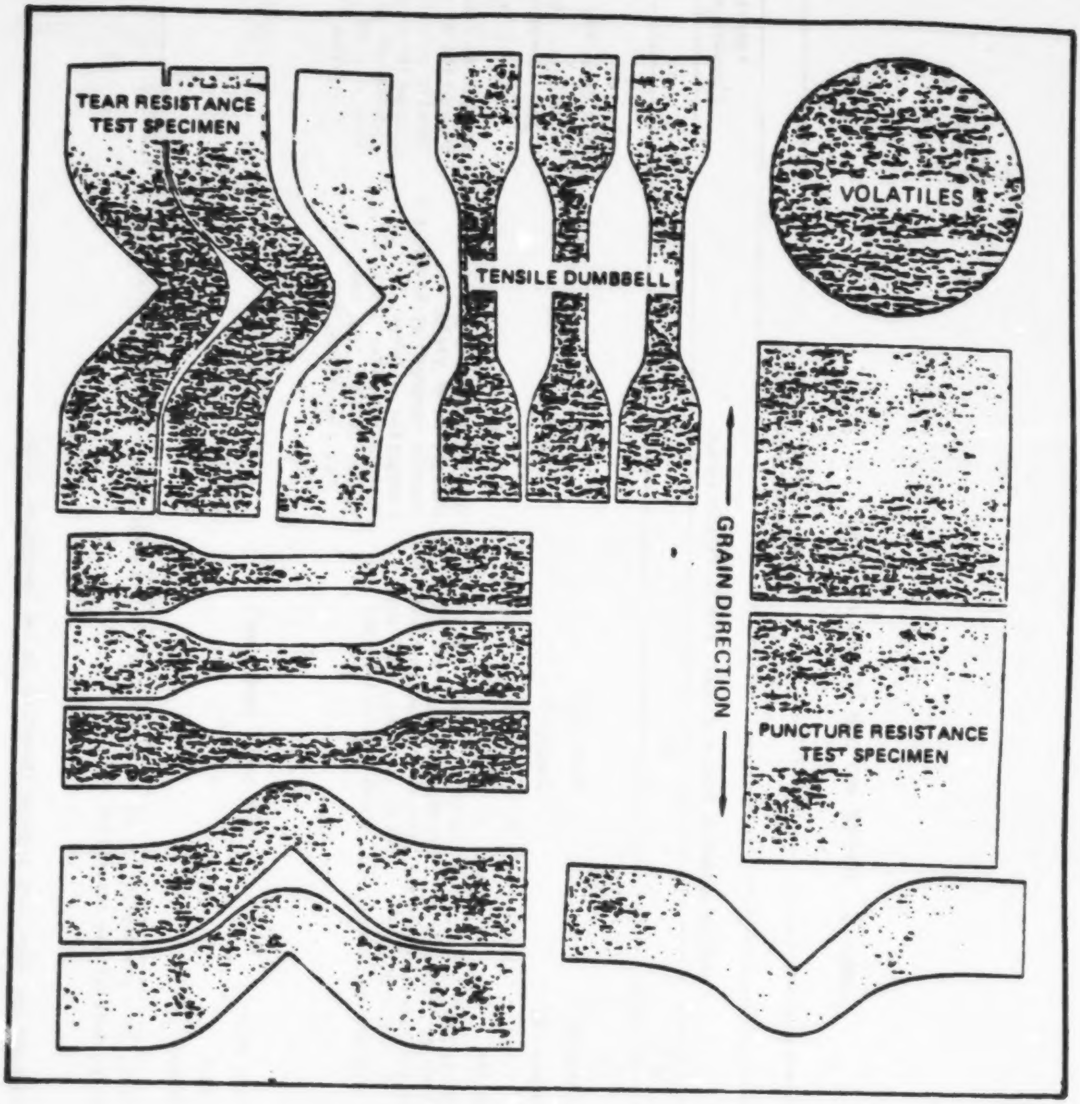
TEAR RESISTANCE TEST SPECIMEN
TENSILE DUMBBELL
VOLATILES
GRAIN DIRECTION
PUNCTURE RESISTANCE TEST SPECIMEN

Figure 1. Suggested pattern for cutting test specimens from nonreinforced, crosslinked, thermoplastic, or crystalline immersed liner samples.

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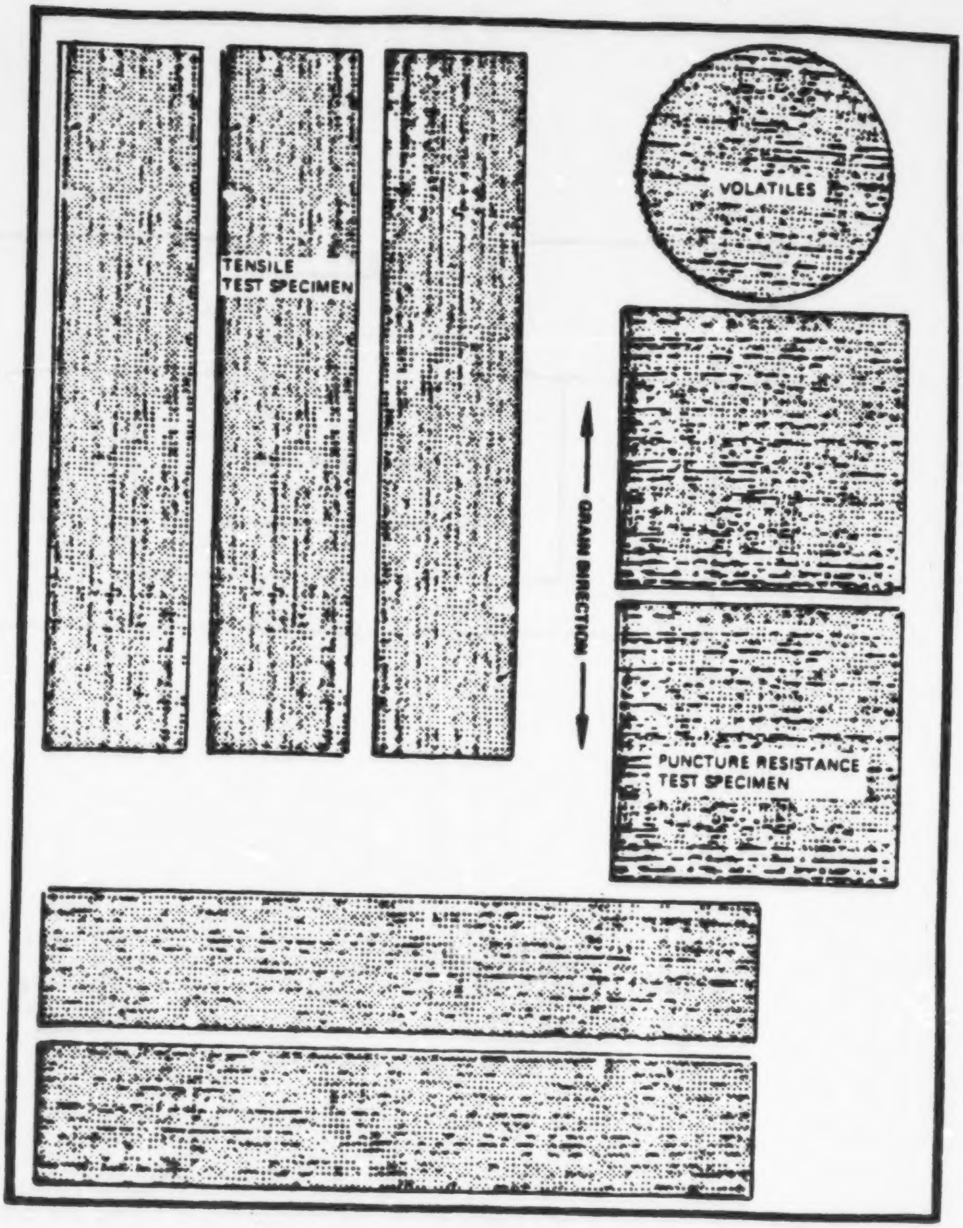
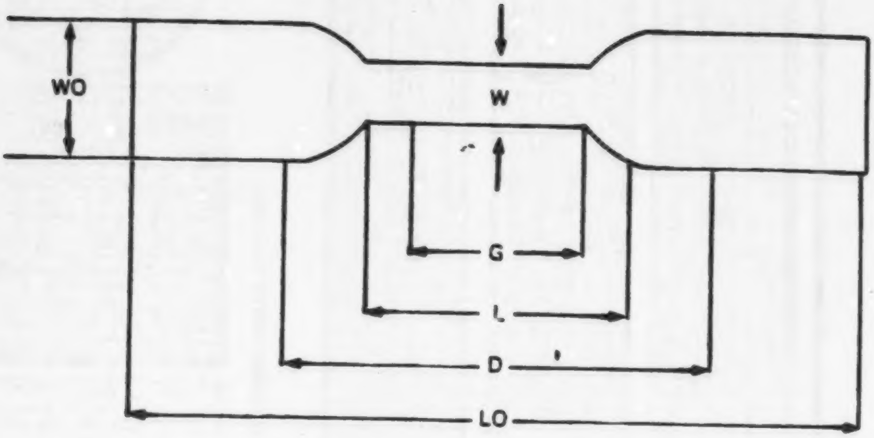

TENSILE
TEST SPECIMEN
VOLATILES
GRAIN DIRECTION
PUNCTURE RESISTANCE
TEST SPECIMEN

Figure 2. Suggested pattern for cutting test specimens from fabric reinforced liner materials. Note: To avoid edge effects, cut specimens 1/8 - 1/4 inch in from edge of immersed sample.



W	-	Width of narrow section	0.25 inches
L	-	Length of narrow section	1.25 inches
WO	-	Width overall	0.625 inches
LO	-	Length overall	3.50 inches
G	-	Gage length	1.00 inches
D	-	Distance between grips	2.00 inches

Figure 3. Die for tensile dumbbell (nonreinforced liners) having the following dimensions.

Do not cut these samples into the shapes shown in Figures 1 or 2 at this time. Samples will be cut into these shapes, as specified in 7.7, after exposure to the waste fluid.

7.4 Label the test specimens and hang in samples of the waste fluid. (It is recommended that different liner materials be immersed in separate tanks to avoid exchange of plasticizers and soluble constituents when plasticized membranes are being tested.) Exposed the test specimens to the stirred waste fluid held at room temperature and 50±2°C.

7.5 At the end of 30, 60, 90, and 120 days of exposure, remove sufficient specimens from waste fluid to determine the membrane's physical properties (see 7.6 and 7.7). Place wet specimen in a labeled container of fresh waste fluid at room temperature for 1 hour to effect coolinfg period before testing. Wipe off as much waste as possible and rinse well with water. Place wet specimen in a labeled polyethylene bag to prevent the specimen from drying out. The specimen should be tested within 24 hour of removal from the immersion.

7.6 To test the immersed specimen, wipe off any remaining waste and rinse with dionized water. Blot specimen dry and measure the following.

1. Gauge thickness, ml or mm.
2. Mass, g.
3. Length, cm.
4. Width, cm.

7.7 Perform the following tests on the exposed specimens. Test for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. See Figure 1 for cutting patterns for non-reinforced liners, and Figure 2 for cutting patterns for reinforced liners.

1. Tear resistance, machine and transverse directions, two specimens each direction for materials without fabric reinforcement.
2. Puncture resistance, two specimens, FTMS 101B, Method 2065. See Figure 1 or 2, as applicable, for sample cutting patterns.
3. Tensile properties, machine and transverse directions, three specimens each direction. See Table 1 for appropriate test method, the recommended test specimen and speed of test, and the values to be reported.
4. Hardness, Duro A (Duro D if Duro A reading is greater than 80), ASTM D2240.

See Figures 1 and 2 for suggested cutting patterns.

7.8 Results and reporting

7.8.1 Plot the curve for each property over the time period 0 to 120 days.

7.8.2 Report all raw, tabulated, and plotted data. Evaluation of the results is described in the documents listed under 6.1, and related agency guidance manuals.

8.0 Quality Control

8.1 Determine the mechanical properties of identical nonimmersed and immersed specimens in accordance with the standard methods for the specific physical property test. Conduct mechanical property tests on nonimmersed and immersed specimens prepared from the same sample or lot of material in the same manner and run under identical conditions. Test immersed specimens immediately after they are removed from the room temperature test solution.

TABLE 2. POLYMERS USED IN FLEXIBLE MEMBRANE LINERS

Thermoplastic Materials (TP)

CPE (Chlorinated polyethylene)[a]
Family of polymers produced by chemical reaction of chlorine on polyethylene. The resulting thermoplastic elastomers contain 25 to 45% chlorine by weight and 0 to 25% crystallinity.

CSPE (Chlorosulfonated polyethylene)[a]
Family of polymers that are produced by polyethylene reacting with chlorine and sulfur dioxide and usually containing 25 to 43% chlorine and 1.0 to 1.4% sulfur.

EIA (Ethylene interpolymer alloy)[a]
A blend of EVA and polyvinyl chloride resulting in a thermoplastic elastomer.

PVC (Polyvinyl chloride)[a]
A synthetic thermoplastic polymer made by polymerizing vinyl chloride.

PVC-CPE (Polyvinyl chloride - chlorosulfonated polyethylene alloy)[a]
A blend of polyvinyl chloride and chlorosulfonated polyethylene.

TN-PVC (Thermoplastic nitrile-polyvinyl chloride)[a]
An alloy of thermoplastic unvulcanized nitrile rubber and polyvinyl chloride.

Vulcanized Materials (XL)

Butyl rubber[a]
A synthetic rubber based on isobutylene and a small amount of isoprene to provide sites for vulcanization.

EPDM (Ethylene propylene diene monomer)[a,b]
A synthetic elastomer based on ethylene, propylene, and a small amount of nonconjugated diene to provide sites for vulcanization.

CM (Crosslinked chlorinated polyethylene)[a]
See chlorinated polyethylene.

CO, ECO (Epichlorohydrin polymers)[a]
Synthetic rubber including two epichlorohydrin-based elastomers which are saturated, high molecular weight aliphatic polyethers with chloromethyl side chains. The two types include homopolymer (CO and a copolymer of epichlorohydrin and ethylene oxide (ECO).

CR (Polychloroprene)[a]
Generic name for a synthetic rubber based primarily on chlorobutadiene.

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[a] Also supplied reinforced with fabric.

[b] Also supplied as a thermoplastic.

TABLE 2. (Continued)

Partially Crystalline Materials (CX)

HDPE (High density polyethylene)
A polymer prepared by the low-pressure polymerization of ethylene as the sole monomer.

HDPE-A (High density polyethylene/rubber alloy)
A blend of high-density polyethylene and rubber.

PE-EP-A (Polyethylene ethylene/propylene alloy)
A blend of polyethylene and poly(ethylene/porpylene).

T-EPDM (Thermoplastic EPDM)
An ethylene-propylene diene monomer blend resulting in a thermoplastic elastomer.

METHOD 9100

SATURATED HYDRAULIC CONDUCTIVITY, SATURATED LEACHATE CONDUCTIVITY, AND INTRINSIC PERMEABILITY METHODS

1.1 Scope and Application

The 9100 method series presents methods available to hydrogeologists and geotechnical engineers for determining the saturated hydraulic and leachate conductivity of naturally occurring and artifically emplaced materials. It is to be used in conjunction with the RCRA, Part 264 guidance documents to satisfy the permitting rules for surface empoundments, landfills, and wastepiles. The manual may also be used in conjunction with the Part 264 permit applications' guidance manual and the Part 264 permit writers' guidance manual to provide the methodologies necessary to assess the hydrologic characteristics of facility sites.

The laboratory tests and field techniques to measure saturated conductivity above the water table outlined in the 9100 method can be used to evaluate any of the following elements that are proposed in an application:

a. Soil liners.

b. Leachate collection and detection layers or units.

c. Soil components of covers.

d. Remolded or engineered soil units, such as berms or dikes, associated with facilities.

The field techniques to measure hydraulic characteristics below the water table can be used as part of a general site investigation, and to meet the standards for groundwater monitoring and environmental performance established in Part 164, Subpart F.

To demonstrate compliance with these standards, a permit applicant must have knowledge of certain aspects of the hydrogeology at the disposal facility, including the hydraulic conductivity of both coarse and fine-grained materials. This knowledge will be necessary when determining appropriate depths for screening monitoring wells at the point of compliance, calculating flow rates, making transport predictions to support alternate concentration limit proposals, and designing corrective action plans. Other methods of determining hydraulic conductivity (including multiple-well tests) that are more suitable to large-scale site investigations are discussed in the permit writer's guidance manual.

The laboratory and field methods that are contained in this method are the most appropriate to meeting the requirements of Part 264 are given in sufficient detail to provide an experienced hydrogeologist or geotechnical engineer with the methodology required to conduct the tests. Additional laboratory and field methods that may be applicable under certain conditions are included by providing reference to standard texts and scientific journals.

Methods for determining unsaturated hydraulic conductivity, which is a function of the degree of liquid saturation, are not included in this manual. The requirements of Subpart F allow only for the use of saturated hydraulic conductivity when making flow rate predictions. However, knowledge of the movement of water, solutes, and leachate in the unsaturated zone may be necessary in designing corrective action plans or supporting alternate concentration limit proposals. Adequate characterization of certain sites may require measurements of unsaturated hydraulic or leachate conductivity. Methods of determining unsaturated conductivity are summarized in a report by Roberts (1982) and references therein.

1.2. Definitions. This section provides definitions of terms used in the remainder of this report. These definitions are taken from U.S. government publications when possible.

1.2.1 Units. This report uses consistent units in all equations. The symbols used are:

Length = L
Mass = M
Time = T

1.2.2 Fluid potential or head is a measure of the potential energy required to move fluid from a point in the porous medium to a reference point. For virtually all situations expected to be found in disposal sites and in groundwater systems, h is defined by the following equation:

$$h = hp + hz \tag{1}$$

where

h = the total fluid potential, expressed as a height of fluid above a reference datum, L.

h_p = the pressure potential caused by the weight of fluid above the point in question, L.

h_p = defined by $h_p = P/\rho g$.

where

P = is the fluid pressure at the point in question, $ML^{-1}T^{-2}$.

ρ = is the fluid density at the prevailing temperature, ML^{-3}.

g = is the acceleration of gravity, LT^{-2}.

h_z = is the height of the point in question above the reference datum, L.

By knowing h_p and h_z at two points along a flow path and by knowing the distance between these points, the fluid potential gradient can be determined.

1.2.3 Hydraulic potential or head is the fluid potential when water is the fluid.

1.2.4 Hydraulic conductivity is the fluid conductivity when water is the fluid. The generic term, fluid conductivity, is discussed below in 1.2.5.

1.2.5 Fluid conductivity is defined as the volume of fluid at the prevailing density and dynamic viscosity that will move in a unit time under a unit fluid potential gradient through a unit area measured at right angles to the direction of flow. It is a property of both the fluid and the porous medium as shown by the following equation:

$$K = \frac{k \rho g}{\mu} \tag{2}$$

where

K = the fluid conductivity, LT^{-1}

k = the intrinsic permeability, a property of the porous medium alone, L^2.

μ = the dynamic viscosity of the fluid at the prevailing temperature, $ML^{-1}\,T^{-1}$.

The fluid conductivity of a porous material is also defined by Darcy's law, which states that the fluid flux (q) through a porous medium is proportional to the first power of the fluid potential across the unit area:

$$q = \frac{Q}{A} = -KI \tag{3}$$

where

q = is the specific fluid flux, LT^{-1}.

Q = is the volumetric fluid flux, L^3T^{-1}.

A = is the cross-sectional area, L^2.

I = is the fluid potential gradient, L^0.

Darcy's law provides the basis for all methods used to determine hydraulic conductivity discussed in this report. The range of validity of Darcy's law is discussed in Section 1.6 (Lohman, 1972).

1.2.6 Leachate conductivity is the fluid conductivity when leachate is in the fluid.

1.2.7 Aquifer is a geologic formation, group of formations, or part of a formation capable of yielding a significant amount of groundwater to wells or springs (40 CFR 260.10).

1.2.8 Confining layer is a body of impermeable material stratigraphically adjacent to one or more aquifers. In nature, however, its hydraulic conductivity may range from nearly zero to some value distinctly lower than that of the aquifer. Its conductivity relative to that of the aquifer it confines should be specified or indicated by a suitable modifier, such as slightly permeable or moderately permeable (Lohman, 1972).

1.2.9 Transmissivity, ($L^2 T^{-1}$), is the rate at which water of the prevailing density and dynamic viscosity is transmitted through a unit width of the aquifer under a unit hydraulic gradient. Although spoken of as a property of the aquifer, the term also includes the saturated thickness of the aquifer and the properties of the fluid. It is equal to an integration of the hydraulic conductivities across the saturated part of the aquifer perpendicular to the flow paths (Lohman, 1972).

1.3. Temperature and viscosity corrections. By using Equation 2, corrections to conditions different from those prevailing during fluid conductivity tests can be made. Two types of corrections can commonly be made: a correction for a temperature that varies from the test temperature, and a correction for fluids other than that used for the test. The temperature correction is defined by:

$$K_f = \frac{K_t \mu_t \rho_f}{u_f \rho_t}, \qquad (4)$$

where

The subscript f refers to field conditions.

t refers to test conditions.

Most temperature corrections are necessary because of the viscosity dependence on temperature. The temperature correction for water can be significant. A temperature decrease from 75° C to 10° C results in a 68% reduction in viscosity and, hence, hydraulic conductivity. Fluid density variations caused by temperature changes are usually very small for most liquids. Equation 4 can also be used to determine hydraulic conductivity if fluids other than water are used. It is assumed, however, when using Equation 4 that the fluids used do not alter the intrinsic permeabilty of the porous medium during the test. Experimental evidence exists that shows that this alteration occurs with a wide range of organic solvents (Anderson and Brown, 1981). Consequently, it is recommended that tests be run using fluids, such as leachates, that might occur at each particular disposal site. Special considerations for using non-aqueous fluids are given in the next section.

1.4. Data interpretation and test selection considerations. Hydraulic conductivity may be determined in wells that are either cased or uncased as described in Section 10. The tests all involve disturbing the existing fluid potential in the tested zone by withdrawal from or injection of fluid into a well either as a slug over an extremely short period of time, or by continuous withdrawal or injection of fluid. The hydraulic conductivity is determined by measuring the response of the water level or pressure in the well as a function of time since the start of the test. Many excellent references are available that give the derivation and use of the methods that are outlined below, including Bouwer (1978), Walton (1970), and Lohman (1972).

The selection of a particular test method and data analysis technique requires the consideration of the purposes of the test, and the geologic framework in which the test is to be run. Knowledge of the stratigraphic relationships of the zone to be tested and both overlying and underlying materials should always be used to select appropriate test design and data interpretation methods.

The equations applied in all computational methods outlined here, and in the above references, are based on idealized models comprising layers of materials of different hydraulic conductivities. The water-level response caused by disturbing the system by the addition or removal of water can be similar for quite different systems. For example, the response of a water-table aquifer and a leaky confined aquifer to pumping can be very similar. Consequently, it is not considered acceptable practice to obtain data from a hydraulic conductivity test and to interpret the type of hydraulic system present without supporting geologic evidence. The Permit Writers Guidance Manual provides additional guidance regarding appropriate aquifer test methods.

The primary use of hydraulic conductivity data from tests described below will usually be to aid in siting monitoring wells for facility design, as well as for compliance with Subpart F of Part 264. As such, the methods are abbreviated to provide guidance in determining hydraulic conductivity only. Additional analyses that may be possible with some methods to define the storage properties of the aquifer are not included.

The well test methods are discussed under the following two categories: (1) methods applicable to coarse-grained materials and tight to extremely tight materials under confined conditions, and (2) methods applicable to unconfined materials of moderate permeability. The single well tests integrate the effects of heterogeneity and anisotropy. The effects of boundaries, such as streams or less permeable materials, usually are not detectable with these methods because of the small portion of the geologic unit that is tested.

1.5. Intrinsic permeability. Rearrangement of Equation 2 results in a definition of intrinsic permeability.

$$k = \frac{K\mu}{\rho g} . \qquad (5)$$

Because this is a property of the medium alone, if fluid properties change, the fluid conductivity must also change to keep the intrinsic permeability constant. By using measured fluid conductivity, and values of viscosity and density for the fluid at the test temperature, intrinsic permeability can be determined.

1.6. Range of validity of Darcy's law. Determination of fluid conductivities using both laboratory and field methods requires assuming the validity of Darcy's law. Experimental evidence has shown that deviations from the linear dependence of fluid flux on the potential gradient exist for both extremely low and extremely high gradients (Hillel, 1971; Freeze and Cherry, 1979). The low gradient limits are the result of the existence of threshold gradients required to initiate flow (Scwartzendruber, 1968). The upper limit for the hydaulic gradient to insure that Darcy's law is valid, is usually established by requiring that the flow through a test cell is laminar (Bear, 1972). Maximum gradients of 10 to 20 are recommended.

If questions arise concerning the validity of Darcy's law, tests can be performed using a range of hydraulic gradients. If a plot of fluid flux versus gradient is linear, Darcy's law can be considered to be valid for the test conditions. In most cases, hydraulic gradients used for hydraulic conductivity tests should be within the range of expected values under actual site operating conditions. For fine-grained materials used for liners and caps, however, use of these gradients may require excessive times to complete the tests. In such cases, higher gradients will be required. The reporting of all hydraulic conductivity data should include the type of test used, and a specification of hydraulic gradients used that are in excess of 10.

1.7 Method classification. Fluid conductivity methods are classified into two divisions: laboratory and field methods. Ideally, compliance with the Part 264 waste-disposal facility requirements should be evaluated by using field methods that test the materials under in-situ conditions whenever possible. In general, field methods can usually provide more representative values than laboratory methods because they test a larger volume of material, thus integrating the effects of macrostructure and heterogeneities. Two types of field methods are included: (1) well or bore hole tests that require the tested interval to be below a water table, and (2) surface or bore hole infiltration tests that may be run on strata above regional or perched water tables. The integrity of liners and covers should not be compromised by the installation of bore holes, piezometers, or infiltrometers required for the tests. These restrictions may result in the requirement to use laboratory tests for determining the fluid conductivity. The transfer value of laboratory data to field conditions can be maximized for compacted liners and covers because it is possible to reconstruct relatively accurately the desired field conditions in the laboratory. However, field conditions that would alter the values determined in the laboratory need to be addressed in permit applications. These conditions include those that would increase conductivity by the formation of microcracks and channels by repeated wetting and drying and by the penetration of roots. For compacted or remolded materials, the applicability of the laboratory values to field conditions depends upon adequate laboratory replication of compaction methods and moisture conditions used in the field.

Laboratory methods are categorized according to the methods used to apply the fluid potential gradient across the sample.

The discussion of the theory, measurement, and computations for tests run under constant and falling-head conditions is followed by a detailed discussion of tests using specific types of laboratory apparatus and the applicability of these tests to remolded compacted, fine-grained uncompacted, and coarse-grained porous media. Section 2.5 is a discussion of the sources of error and guidance for establishing the precision of laboratory tests. Method 9106 provides a discussion of the special considerations for conducting laboratory tests using non-aqueous permeants.

Field methods are limited to those requiring a single bore hole, piezometer, or infiltrometer. Methods requiring multiple bore holes or piezometers and areal methods are included by reference. General methods for fractured media are given in Section 3.8. A discussion of the important considerations in well installation, construction, and development is included in Section 3.0 of Method 9100.

2.0 Laboratory Methods

2.1 Sample collection for laboratory methods. To assure that a reasonable assessment is made of field conditions at a disposal site, a site investigation plan should be developed to direct sampling and analysis. This plan generally requires the professional judgment of an experienced hydrogeologist or geotechnical engineer. General guidance is provided for plan development in the Guidance Manual for Preparation of a Part 264 Land Disposal Facility Permit Application (EPA, in press). The points listed below should be followed:

a. The hydraulic conductivity of a soil liner should be determined either from samples that are processed to simulate the actual liner, or from an undisturbed sample of the complete liner.

To obtain undisturbed samples, the thin-walled tube sampling method (ASTM Method #D1587-74) or a similar method may be used. Samples representative of each lift of the liner should be obtained, and used in the analyses. If actual undisturbed samples are not used, the soil used in liner construction must be processed to represent accurately the liner's initial water content and bulk density. The method described in Section 6.3 or ASTM Method #D698-70 (ASTM, 1978) can be used for this purpose.

b. For purposes of the general site investigation, the general techniques presented in ASTM Method #D420-69 (ASTM, 1978) should be followed. This reference establishes practices for soil and rock investigation and sampling, and incorporates various detailed ASTM procedures for investigations, sampling, and material classification.

2.2 Constant-head methods (Section 4.0). The constant-head method is the simplest method to determine hydraulic conductivity of saturated soil samples. The concept of the constant-head method is schematically illustrated in Figure 1. The inflow of fluid is maintained at a constant head (h) above a datum and outflow (Q) is measured as a function of time (t). Using Darcy's law, the hydraulic conductivity can be determined using the following equation after the outflow rate has become constant:

$$K = QL/hA \qquad (6)$$

where

K = hydraulic conductivity (LT^{-1}).

L = length of sample, L.

A = cross-sectional area of sample, L^2.

Q = outflow rate, L^3T^1.

h = fluid head difference across the sample, L.

Constant-head methods should be restricted to tests on media having high fluid conductivity.

2.3 Falling-head methods (Section 5.0). A schematic diagram of the apparatus for the falling-head method is shown in Figure 2. The head of inflow fluid decreases from h_0 to h_1 as a function of time (t) in a standpipe directly connected to the specimen. The fluid head at the outflow is maintained constant. The quantity of outflow can be measured, as well as the quantity of inflow. For the setup shown in Figure 2a, the hydraulic conductivity can be determined using the following equation:

$$K = \frac{2.3\ aL}{At} \log_{10} \frac{h_0}{h_1} \qquad (7)$$

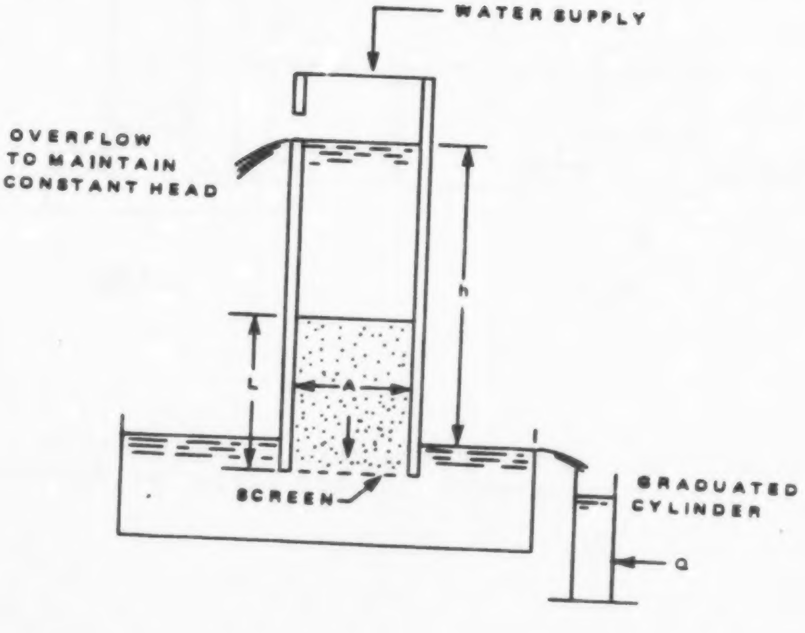

WATER SUPPLY
OVERFLOW TO MAINTAIN CONSTANT HEAD
h
L
A
SCREEN
GRADUATED CYLINDER
Q

Figure 1.--Principle of the constant head method

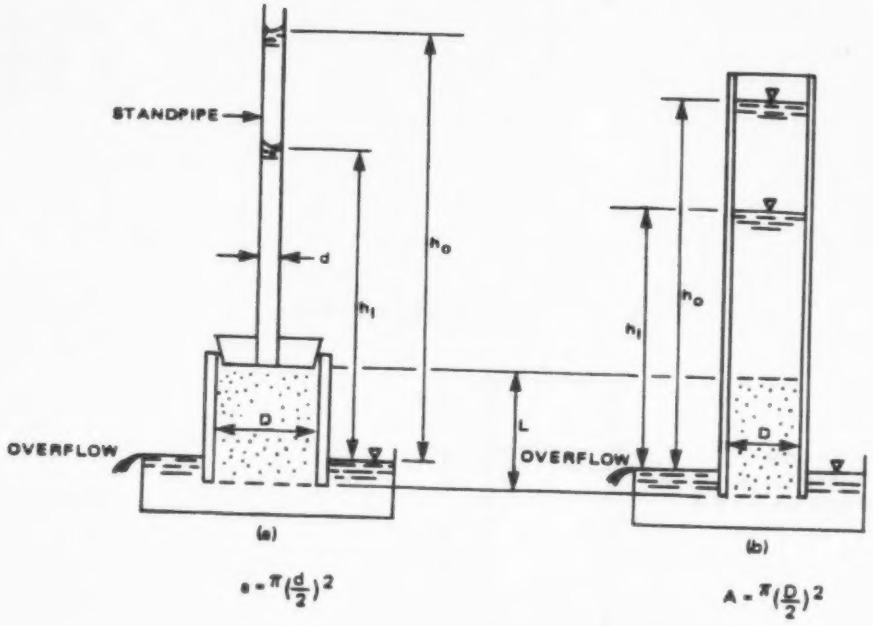

STANDPIPE
d
h_o
h_1
D
L
OVERFLOW
OVERFLOW
h_1
h_o
D
(a)
(b)
$a = \pi(\frac{d}{2})^2$
$A = \pi(\frac{D}{2})^2$

Figure 2.--Principle of the falling head method using a small (a) and large (b) standpipe.

where

a = the cross-sectional area of the standpipe, L^2.

A = the cross-sectional area of the specimen, L^2.

L = the length of the specimen, L.

t = elapsed time from t_1 to t_2, T.

For the setup shown in Figure 2b, the term a/A in Equation 9 is replaced by 1.0. Generally, falling head methods are applicable to fine-grained soils because the testing time is less than constant head methods, and because the low flow rates are more readily observed with the falling head than the constant head methods.

2.4 General test considerations

2.4.1 Fluid supplies to be used. For determining hydraulic conductivity and leachate conductivity, the supplies of permeant fluid used should be de-aired. Air coming out of solution in the sample can significantly reduce the measured fluid conductivity. De-airing can be achieved by boiling the water supply under a vacuum, bubbling helium gas through the supply, or both.

Significant reductions in hydraulic conductivity can also occur in the growth and multiplication of microorganisms present in the sample. If it is desirable to prevent such growth, a bactericide or fungicide, such as 2,000 ppm formaldehyde, or 1,000 ppm phenol (Olsen and Daniel, 1981) can be added to the fluid supply. Distilled water should never be used for determining hydraulic conductivity in the laboratory. Native groundwater from the aquifer underlying the sampled area or water prepared to simulate the native groundwater chemistry should be used.

2.4.2 Pressure and fluid potential measurement. The equations in this report are all dimensionally correct; that is, any consistent set of units may be used for length, mass, and time. Consequently, measurements of pressure and/or fluid potential using pressure gauges and manometers must be reduced to the consistent units used before applying either Equation 8 or 9. Pressures or potentials should be measured to within a few tenths of one percent of the gradient applied across the sample.

2.5 Sources of error for laboratory test for hydraulic conductivity. There are numerous potential sources of error in laboratory tests for hydraulic conductivity. Table 1 summarizes some potential errors that can occur. Olson and Daniel (1981) provide a more detailed explanation of sources of these errors and methods to minimize them. If the hydraulic conductivity does not fall within the expected range for the soil type, as given in Table 2, the measurement should be repeated after checking the source of error in Table 1.

TABLE 1. SUMMARY OF PUBLISHED DATA ON POTENTIAL ERRORS IN USING DATA FROM LABORATORY PERMEABILITY TESTS ON SATURATED SOILS

Source of error and references	Measured K Too low or too high?
1. Voids Formed in Sample Preparation (Olson and Daniel, 1981).	High
2. Smear Zone Formed During Trimming (Olson and Daniel, 1981).	Low
3. Use of Distilled Water as a Permeant (Fireman, 1944; and Wilkinson, 1969).	Low
4. Air in Sample Resulting From Incomplete Saturation (Johnson, 1954).	Low
5. Growth of Micro-organisms (Allison, 1947).	Low
6. Use of Excessive Hydraulic Gradient (Schwartzendruber, 1968; and Mitchell and Younger, 1967).	Low or High
7. Use of Temperature Other than the Test Temperature	Varies
8. Ignoring Volume Change Due to Stress Change (no confining pressure used).	High
9. Performing Laboratory Rather than In-Situ Tests (Olson and Daniel, 1981).	Usually low
10. Impedance Caused by the Test Apparatus, Including the Resistance of the Screen or Porous Stone Used to Support the Sample (Olson and Daniel, 1981).	Low

TABLE 2. HYDRAULIC CONDUCTIVITIES ESTIMATED FROM GRAIN SIZE DESCRIPTIONS (x 10^{-3} cm sec^{-1})

Grain size class or range from sample description	Degree of sorting			Silt content		
	Poor	Moderate	Well	Slight	Moderate	High
Fine-Grained Materials						
Clay			<.0004			
Silt, clayey			0.4-1			
Silt, slightly sandy			2			
Silt, moderately sandy			2-3			
Silt, very sandy			3-4			
Sandy silt			4			
Silty sand			5			
Sands and Gravels[a]						
Very fine sand	5	7	10	8	7	5
Very fine to fine sand	10	10	-	9	7	5
Very fine to medium sand	13	15-17	-	11	10	7
Very fine to coarse sand	17	-	-	14	11	9
Very fine to very coarse sand	21	-	-	18	14	10
Very fine sand to fine gravel	27	-	-	24	18	13
Very fine sand to medium gravel	35	-	-	28	23	17
Very fine sand to coarse gravel	45	-	-	38	30	23
Fine sand	10	14	19	12	10	7
Fine to medium sand	19	24	-	17	14	11
Fine to coarse sand	20	23-25	-	19	15	11
Fine to very coarse sand	25	-	-	21	17	12
Fine sand to fine gravel	31	-	-	26	21	16
Fine sand to medium gravel	40	-	-	33	26	20
Fine sand to coarse gravel	51	-	-	38	31	25
Medium sand	24	28	33	23	18	14
Medium to coarse sand	26	33	-	25	20	15
Medium to very coarse sand	30	35-39	-	25	22	17
Medium sand to fine gravel	36	-	-	30	24	18
Medium sand to medium gravel	46	-	-	40	29	23
Medium sand to coarse gravel	58	-	-	47	38	29
Coarse sand	28	38	47	33	26	19
Coarse to very coarse sand	33	47	-	33	26	20
Coarse sand to fine gravel	41	48-55	-	38	31	24
Coarse sand to medium gravel	52	-	-	40	33	26
Coarse sand to coarse gravel	65	-	-	47	35	32
Very coarse sand	38	52	66	40	33	26
Very coarse sand to fine gravel	47	76	-	42	37	31
Very coarse sand to medium gravel	60	70-80	-	52	43	35
Very coarse sand to coarse gravel	73	-	-	56	47	37
Fine gravel	56	76	94	80	49	36
Fine to medium gravel	71	118	-	71	59	47
Fine to coarse gravel	86	102-118	-	83	67	51
Medium gravel	85	82	141	85	71	56
Medium to coarse gravel	104	165	-	104	86	67
Coarse gravel	118	165	213	118	100	83

[a] Reduce by 10 percent if grains are subangular.

Source: Lappala (1978).

3.0 Field Methods

This section discusses methods available for the determination of fluid conductivity under field conditions. Two types of field tests are discussed in this section. The first type utilizes wells, bore holes, or piezometers in which the tested interval is below the water table. These tests are applicable to a wide range of lithologies. The second type of test is applicable for testing the saturated conductivity of materials that are above perched or regional water tables. As most of these tests will use water as the testing fluid, either natural formation water or water added to a bore hole, piezometer, or infiltrometer, the term hydraulic conductivity will be used for the remainder of this section. However, if field tests are run with leachate or other fluids, the methods are equally applicable.

3.1 Well, piezometer, and bore hole tests. The location of wells, selection of screened intervals, and the appropriate tests that are to be conducted depend upon the specific site under investigation. The person responsible for such selections should be a qualified hydrogeologist or geotechnical engineer who is experienced in the application of established principles of contaminant hydrogeology and groundwater hydraulics. The following are given as general guidelines.

a. The bottom of the screened interval should be below the lowest expected water level.

b. Wells should be screened in the lithologic units that have the highest probability either of receiving contaminants or conveying them down gradient.

c. Wells up gradient and down gradient of sites should be screened in the same lithologic unit.

Standard reference texts on groundwater hydraulics and contaminant hydrogeology that should be consulted include: Bear (1972), Bouwer (1978), Freeze and Cherry (1979), Stallman (1971), and Walton (1970).

The success of using field methods to determine hydraulic conductivity is often determined by the design, construction, and development of the well or bore hole used for the tests. Details of these methods are beyond the scope of this report; however, important considerations are given in Sections 3.1 and 3.2. Detailed discussions of well installation, construction, and development methods are given by Bouwer (1978), pages 160-180, Acker (1974), and Johnson (1972).

The purpose of using properly constructed wells for hydraulic conductivity testing is to ensure that test results reflect conditions in the materials being investigated, rather than the conditions caused by well construction. Misinterpretation of field results may also occur if the wells are screened in units other than those being tested. In all cases, diagrams showing all details of the actual well or bore hole constructed for the test should be prepared and included as part of reports on site characterization.

The analytical solutions, used in the interpretation of field tests, describe the response of an idealized representation of an actual geologic configuration. The aquifer to be studied, however, may be heterogenous and/or an isotropic reflecting complex geologic processes. Any prediction based on such analytical expressions must be regarded as a best estimate of actual hydrologic conditions. This problem is compounded if the stratigraphy of an area is unknown so that few corrections can be made to approximate actual field conditions.

3.1.1 Well installation methods. Well installation methods are listed below in order of preference for groundwater testing and monitoring. The order was determined by the need to minimize side-wall plugging by drilling fluids and to maximize the accurate detection of saturated zones. This order should be used as a guide, combined with the judgment of an experienced hydrogeologist, in selecting a drilling method. The combined uses of wells for hydraulic conductivity testing, water-level monitoring, and water-quality sampling for organic contaminants were considered in arriving at the ranking.

a. Hollow-stem auger.

b. Cable tool.

c. Air rotary.

d. Rotary drilling with non-organic drilling fluids.

e. Air foam rotary.

f. Rotary with organic based drilling fluids.

Although the hollow stem-auger method is usually preferred for the installation of most shallow wells (less than 100 feet), care must be taken if the tested zone is very fine. Smearing of the bore hole walls by drilling action can effectively seal off the bore hole from the adjacent formation. Scarification can be used to remedy this.

3.1.2 Wells requiring well screens. Well screens placed opposite the interval to be tested should be constructed of materials that are compatible with the fluids to be encountered. Generally, an inert material is preferred for groundwater contamination studies. The screen slot size should be determined to minimize the inflow of fine-grained material to the well during development and testing. Bouwer (1978) and Johnson (1972) give a summary of guidelines for sizing well screens.

The annulus between the well screen and the bore hole should be filled with an artificial gravel pack or sand filter. Guidelines for sizing these materials are given by Johnson (1972). For very coarse materials, it may be acceptable to allow the materials from the tested zone to collapse around the screen, forming a natural gravel pack.

The screened interval should be isolated from overlying and underlying zones by materials of low hydraulic conductivity. Generally, a short bentonite plug is placed on top of the material surrounding the screen, and cement grout is placed in the bore hole to the next higher screened interval, in the case of multiple screen wells, or to the land surface for single screen wells.

Although considerations for sampling may dictate minimum casing and screen diameters, the recommended guideline is that wells to be tested by pumping, bailing, or injection in coarse-grained materials should be at least 4 inches inside diameter. Wells to be used for testing materials of low hydraulic conductivity by sudden removal or injection of a known volume of fluid should be constructed with as small a casing diameter as possible to maximize measurement resolution of fluid level changes. Casing sizes of 1.25 to 1.50 inches usually allow this resolution while enabling the efficient sudden withdrawal of water for these tests.

3.1.3 Wells not requiring well screens. If the zone to be tested is sufficiently indurated that a well screen and casing is not required to prevent caving, then it is preferable to use a bore hole open to the zone to be tested. These materials generally are those having low to extremely low hydraulic conductivities. Consolidated rocks having high conductivity because of the presence of fractures and solution openings may also be completed without the use of a screen and gravel pack. Uncased wells may penetrate several zones for which hydraulic conductivity tests are to be run. In these cases, the zones of interest can be isolated by the use of inflatable packers.

3.2 Well development. For wells that are constructed with well screens and gravel packs, and for all wells in which drilling fluids have been used that may have penetrated the materials to be tested, adequate development of the well is required to remove these fluids and to remove the fine-grained materials from the zone around the well screen. Development is carried out by methods such as intermittent pumping, jetting with water, surging, and bailing. Adequate development is required to assure maximum communication between fluids in the borehole and the zone to be tested. Results from tests run in wells that are inadequately developed will include an error caused by loss of fluid potential across the undeveloped zone, and computed hydraulic conductivities will be lower than the actual value. Bouwer (1978) and Johnson (1972) give further details on well development including methods to determine when adequate development has occurred.

3.3 Single well tests. The tests for determining hydraulic conductivity with a single well discussed below are applicable for confined and unconfined conditions. The methods are usually called slug tests because the test involves removing a slug of water instantaneously from a well and measuring the recovery of water in the well. The method was first developed by Hvorslev (1951), whose analysis did not consider the effect of fluid stored in the well. Cooper and others (1967) developed a method that considers well bore storage. However, their method only applied to wells that are open to the entire zone to be tested and that tap confined aquifers. Because of the rapid water-level response in coarse materials, the tests are generally limited to zones with a transmissivity of less than about 70 cm^2/sec (Lohman, 1972). The method has been extended to allow testing of extremely tight formations (Bredehoeft and Papadopulos, 1980). Bouwer and Rice (1976) developed a method for analyzing slug tests for unconfined aquifers.

3.4 Multiple well tests. Hydraulic conductivity can also be determined by conventional pumping tests in which water is continuously withdrawn or injected using one well, and the water-level response is measured over time in or near more observation wells. These methods generally test larger portions of aquifers than the single well tests discussed in Sections 10, 11, and 12 and are more appropriate for obtaining data for large-scale site investigations to meet the requirements of Part 264, Subpart F. The following references give excellent discussions of the design and interpretation of these tests: Lohman (1972), Stallman (1971), and Walton (1970).

3.5 Estimates of hydraulic conductivity for coarse-grained materials. To characterize the groundwater flow system and satisfy the intent of Part 264, Subpart F, estimates of the hydraulic conductivity based on grain-size analyses or visual grain-size classification may be appropriate. However, hydraulic conductivities determined by these methods ar enot to be used in permit applications in the absence of actual measuremnets. Several theoretical models are available to provide these estimates, with one of the most widely used being the Kozeny-Carmen equation, which defines the intrinsic permeability, as adapted from Bear (1972):

$$k = \frac{n^3}{(1-n)^2} \quad \frac{D_{50}{}^2}{180} \qquad (8)$$

where n is the effective porosity and all other terms are as previously defined.

An empirical approach that has been used by the U.S. Geological Survey (Lappala, 1978) in several studies relates conductivity determined by aquifer testing to grain size, degree of sorting, and silt content. Table 2 provides the estimates of hydraulic conductivity.

3.6 Measurement of saturated hydraulic conductivity above the water table. The field determination of saturated hydraulic or leachate conductivity may be required for strata that are not initially saturated with water. These strata would include natural or compacted clays used for liners or caps that lie above the water table. Conductivities determined in the laboratory on undisturbed or recompacted cores may be as much as two or three orders of magnitude less than field values determined by infiltration tests over large areas (Daniel, 1981; Olson and Daniel, 1981). The reason for the discrepancy is usually the presence of such features as vertical microcracks from wetting and drying, and channels or macropores along live or decayed root systems. Consequently, field tests may be required to verify laboratory values in some cases.

Two field methods are presented in this section to determine saturated hydraulic conductivity above the water table: (1) the air entry permeameter method, and (2) the double tube infiltrometer method. Both methods rely upon the establishment of saturated, vertical flow in the strata being tested. The establishment of such flow may require periods of several days or weeks in some fine grained materials.

3.7 Fractured media. Determining the hydraulic properties of fractured media is always a difficult process. Unlike porous media, Darcy's law may not be directly applicable to flow-through fractures, although it often can be applied empirically to large bodies of fractured rock that incorporate many fractures. Describing local flow conditins in fractured rock often poses considerable difficulty. Sowers (1981) discusses determinations of hydraulic conductivity in rock. This reference should be consulted for guidance in analyzing flow-through fractured media.

Fine-grained sediments, such as glacial tills, are commonly fractured in both saturated and unsaturated settings. These fractures may be sufficiently interconnected to have a significant influence on groundwater flow, or they may be of very limited connection and be of little practical significance.

Frequently, a laboratory test of a small sample of clay will determine hydraulic conductivity to be on the order of 10^{-8} cm/sec. A piezometer test of the same geologic unit over an interval containing fractures may determine a hydraulic conductivity on the order of perhaps 10^{-5} or 10^{-6} cm/sec. To assess the extent of fracture interconnection, and hence the overall hydraulic conductivity of the unit, several procedures can be used. Closely spaced piezometers can be installed: one can be used as an observation well while water is added to or withdrawn from the other. Alternately, a tracer might be added to one piezometer, and the second piezometer could be monitored. These, and other techniques are discussed by Sowers (1981). Infiltrometer (Section 14) and air entry permeameter (Section 13) methods also may be used for fractured, unconsolidated materials, such as clays or fills.

For situations that may involve flow-through fractured media, it is important to note in permit applications that an apparent hydraulic conductivity determined by tests on wells that intersect a small number of fractures may be several orders of magnitude lower or higher than the value required to describe flow-through parts of the groundwater system that involve different fractures and different stress conditions from those intercepted during the test.

4.0 Constant-Head Test with Conventional Permeameter

4.1 Scope and Application

This method covers the determination of the hydraulic conductivity of soils by a constant-head method using a conventional permeameter. This method should be restricted to disturbed coarse-grained soils. If this method is to be used for fine-grained soils, the testing time may be prohibitively long. This method was taken from the Engineering and Design, Laboratory Soils Testing Manual (U.S. Army, 1980). It parallels ASTM Method D2434-68 (ASTM, 1978). The ASTM method gives extensive discussion of sample preparation and applicability and should be reviewed before conducting constant-head tests. Lambe (1951) provides additional information on sample preparation and equipment procedure.

4.2 Apparatus

The apparatus is shown schematically in Figure 3. It consists of the following:

a. A permeameter cylinder having a diameter at least 8 times the diameter of the largest particle of the material to be tested.

b. Constant-head filter tank.

c. Perforated metal disks and circular wire to support the sample.

d. Filter materials that have a permeability at least an order of magnitude other than the sample to be tested, such as coarse sand or gravel.

e. Manometers connected to the top and bottom of the sample.

f. Graduated cylinder.

g. Thermometer.

h. Stop watch.

i. De-aired water.

j. Balance sensitive to 0.1 gram.

k. Drying oven.

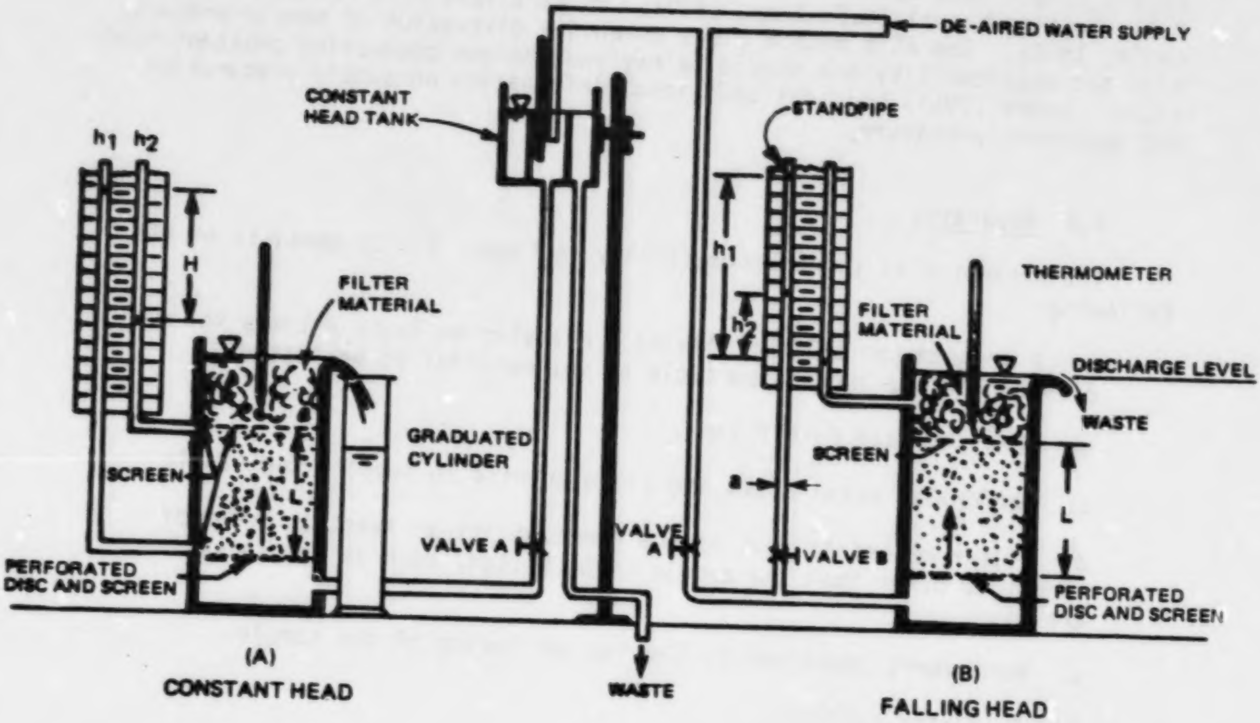

DE-AIRED WATER SUPPLY
CONSTANT HEAD TANK
STANDPIPE
h_1
h_2
H
FILTER MATERIAL
THERMOMETER
FILTER MATERIAL
h_1
h_2
DISCHARGE LEVEL
WASTE
SCREEN
GRADUATED CYLINDER
SCREEN
a
L
L
VALVE A
VALVE A
VALVE B
PERFORATED DISC AND SCREEN
PERFORATED DISC AND SCREEN
(A)
CONSTANT HEAD
WASTE
(B)
FALLING HEAD

FIGURE 3 APPARATUS SETUP FOR THE CONSTANT HEAD (A) AND FALLING HEAD (B) METHODS

4.3 Procedures

4.3.1 Sample preparation

4.3.1.1 The amount of material should be sufficient to provide a specimen in the permeameter having a minimum length of about one to two times the diameter of the specimen.

4.3.1.2 Place a wire screen, with openings small enough to retain the specimen, over a perforated disk near the bottom of the permeameter above the inlet. The screen openings should be approximately equal to the 10% finer size of the specimen for coarse-grained samples.

4.3.1.3 Allow de-aired water to enter the water inlet of the permeameter to a height of about 1/2 in. above the bottom of the screen, taking care that no air bubbles are trapped under the screen.

4.3.1.4 Mix the material thoroughly and place in the permeameter to avoid segregation. The material should be dropped just at the water surface, keeping the water surface about 1/2 in. above the top of the soil during placement. A funnel or a spoon is convenient for this purpose.

4.3.1.5 The placement procedure outlined above will result in a saturated specimen of uniform density although in a relatively loose condition. To produce a higher density in the specimen, the sides of the permeameter containing the soil sample are tapped uniformly along its circumference and length with a rubber mallet to produce an increase in density; however, extreme caution should be exercised so that fines are not put into suspension and segregated within the sample. As an alternative to this procedure, the specimen may be placed using an appropriate sized funnel or spoon. Compacting the specimen in layers is not recommended because a film of dust may be formed at the surface of the compacted layer, which might affect the permeability results. After placement, apply a vacuum to the top of the specimen and permit water to enter the evacuated specimen through the base of the permeameter.

4.3.1.6 After the specimen has been placed, weigh the excess material, if any, and the container. The specimen weight is the difference between the original weight of sample and the weight of the excess material. Care must be taken so that no material is lost during placement of the specimen. If there is evidence that material has been lost, oven-dry the specimen after the test and weigh as a check.

4.3.1.7 Level the top of the specimen, cover with a wire screen similar to that used at the base, and fill the remainder of the permeameter with a filter material. If smearing occurs during leveling, some scarification of the smeared surface should be done.

4.3.1.8 Measure the length of the specimen, inside diameter of the permeameter, and distance between the centers of the manometer tubes (L) where they enter the permeameter.

4.3.2 Test procedure

4.3.2.1 Adjust the height of the constant-head tank to obtain the desired hydraulic gradient. Hydraulic gradients ranging from 0.2 to 0.5 are recommended. Too high a hydraulic gradient may cause turbulent flow and also result in piping of soils. In general, coarser soils require lower hydraulic gradients. See Section 1.5 of Method 9100 for further discussion of excessive gradients.

4.3.2.2 Open valve A (see Figure 3a) and record the initial peizometer readings after the flow has become stable. Exercise care in building up heads in the permeameter so that the specimen is not disturbed.

4.3.2.3 After allowing a few minutes for equilibrium conditions to be reached, measure by means of a graduated cylinder the quantity of discharge corresponding to a given time interval. Measure the piezometric heads (h_1 and h_2) and the water temperature in the permeameter.

4.3.2.4 Record the quantity of flow, piezometer readings, water temperature, and the time interval during which the quantity of flow was measured.

4.3.3 Calculations. By plotting the accumulated quantity of outflow versus time on rectangular coordinate paper, the slope of the linear portion of the curve can be determined, and the hydraulic conductivity can be calculated using the following equation:

$$K = QL/hA \qquad (1)$$

where

K = hydraulic conductivity, LT^{-1}.

L = length of sample, L.

A = cross-sectional area of sample, L^2.

Q = outflow rate, L^3T^1.

h = $h_1 - h_2$.

5.0 Falling Head Test with Conventional Permeameter

5.1 Scope and Application

The falling head test can be used for all soil types, but is usually most widely applicable to materials having low permeability. Compacted, remolded, fine-grained soils can be tested with this method. The method presented is taken from the Engineering and Design, Laboratory Soils Testing Manual (U.S. Army, 1980).

5.2 Apparatus

The schematic diagram of falling head permeameter is shown in Figure 3. The permeameter consists of the following equipment:

a. Permeameter cylinder - a transparent acrylic cylinder having a diameter at least 8 times the diameter of the largest particles.

b. Porous disk.

c. Wire screen.

d. Filter materials.

e. Manometer.

f. Timing device.

g. Thermometer.

5.3 Procedure

5.3.1 Sample preparation. Sample preparation for coarse-grained soils is similar to that described previously in Section 4. For fine-grained soils, samples are compacted to the desired density using methods described in ASTM Method D698-70.

5.3.2 Test procedure

5.3.2.1 Measure and record the height of the specimen, L, and the cross-sectional area of the specimen, A.

5.3.2.2 With valve B open (see Figure 3b), crack valve A, and slowly bring the water level up to the discharge level of the permeameter.

5.3.1.3 Raise the head of water in the standpipe above the discharge level of the permeameter. The difference in head should not result in an excessively high hydraulic gradient during the test. Close valves A and B.

5.3.1.4 Begin the test by opening valve B. Start the timer. As the water flows through the specimen, measure and record the height of water in the standpipe above the discharge level, h_1, at time t_1, and the height of water above the discharge level, h_2 at time t_2.

5.3.1.5 Observe and record the temperature of the water in the permeameter.

5.3.3 Calculations. From the test data, plot the logarithm of head versus time, on rectangular coordinate paper or use semilog paper. The slope of the linear part of the curve is used to determine

$$\frac{\log_{10}(h_1/h_2)}{t}$$

Calculate the hydraulic conductivity using the following equation:

$$k = \frac{2.3\ aL}{At}\ \log_{10}\frac{h_0}{h_1} \tag{1}$$

where

a = the cross-sectional area of the standpipe, L^2.

A = the cross-sectional area of the specimen, L^2.

L = the length of the specimen, L.

t = elapsed time from t_1 to t_2, T.

For the setup shown in Figure 2b, the term a/A in the equation is replaced by 1.0. Generally, falling head methods are applicable to fine-grained soils because the testing time is less than constant head methods, and because the low flow rates are more readily observed with the falling head than the constant head methods.

6.0 Modified Compaction Permeameter Method

6.1 Scope and Application

This method can be used to determine the hydraulic conductivity of a wide range of materials. The method is generally used for remolded fine-grained soils and under constant head conditions. The method was taken from Anderson and Brown (1981) and EPA (1980).

6.2 Apparatus

The apparatus is shown in Figure 4 and consists of the equipment and accessories as follows:

6.2.1 Soil chamber - a compaction mold having a diameter 8 times larger than the diameter of the largest particles. Typically, ASTM standard mold (Number CN405) is used.

6.2.2 Fluid chamber - a compaction mold sleeve having the same diameter as the soil chamber.

6.2.3 2 kg hammer.

6.2.4 Rubber rings used for sealing purposes.

6.2.5 A coarse porous stone having a permeability at least one order of magnitude higher than the tested sample.

6.2.6 Regulated source of compressed air.

6.2.7 Pressure gauge or manometer to determine the pressure on the fluid chamber.

6.3 Procedures

6.3.1 Sample Preparation

6.3.1.1 Obtain sufficient representative soil sample. Air dry the sample at room temperature. Do not oven dry.

6.3.1.2 Thoroughly mix the selected representative sample with water to obtain a desired moisture content.

6.3.1.3 Compact the sample to the desired density within the mold using the method described as part of ASTM Method D698-70.

9100/26

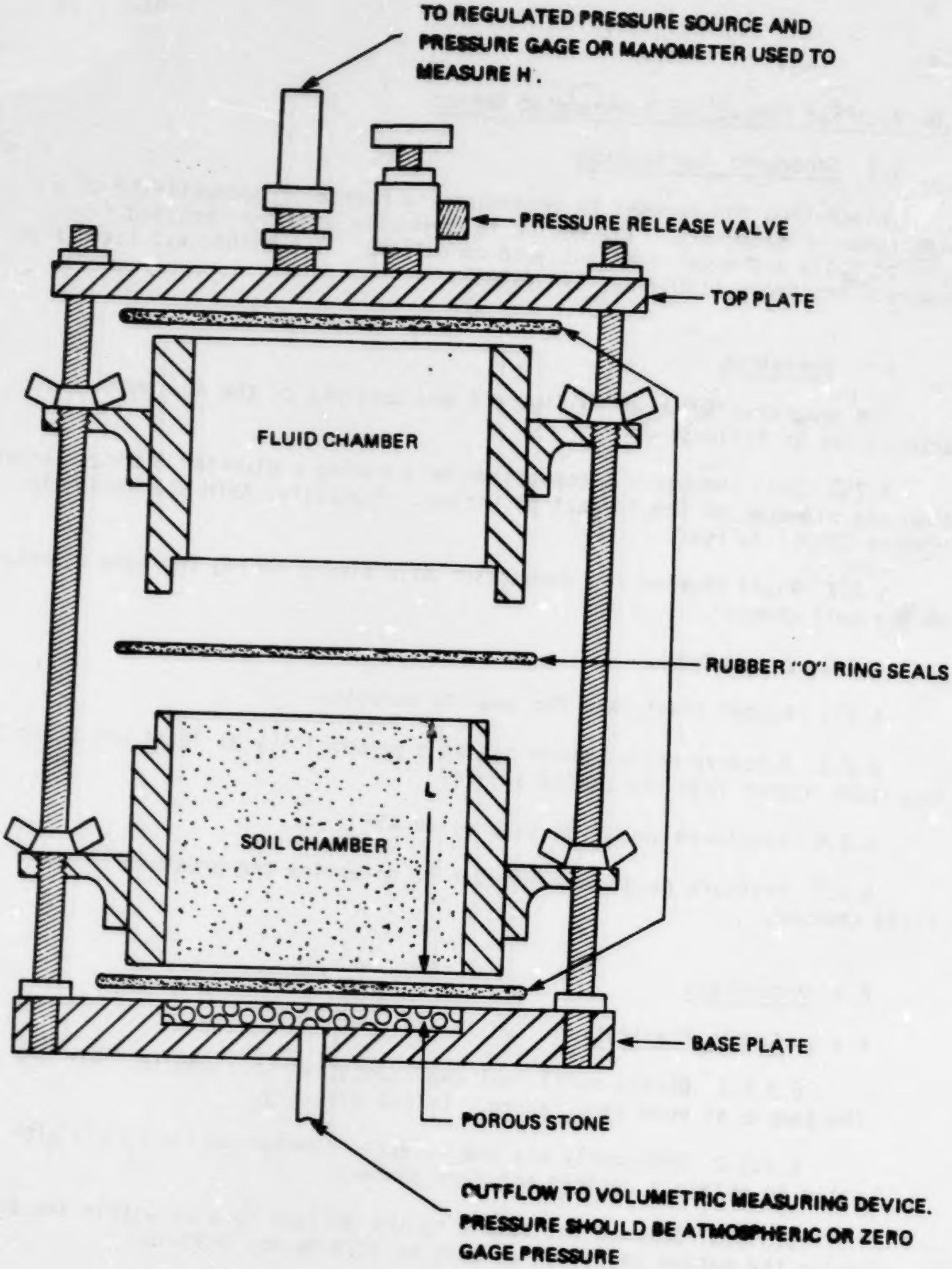

TO REGULATED PRESSURE SOURCE AND PRESSURE GAGE OR MANOMETER USED TO MEASURE H.
PRESSURE RELEASE VALVE
TOP PLATE
FLUID CHAMBER
RUBBER "O" RING SEALS
L
SOIL CHAMBER
BASE PLATE
POROUS STONE
OUTFLOW TO VOLUMETRIC MEASURING DEVICE. PRESSURE SHOULD BE ATMOSPHERIC OR ZERO GAGE PRESSURE

Figure 4.--Modified compaction permeameter. Note: h in Equation 8 is the difference between the regulated inflow pressure and the outflow pressure. Source: Anderson and Brown, 1981.

6.3.1.4 Level the surface of the compacted sample with straight edge and weigh.

6.3.1.5 Measure the length and diameter of the sample, and determine the density using the dimensions and the sample weight.

6.3.1.6 Assemble the apparatus, make sure that there are no leaks, then connect the pressure line to the apparatus.

6.3.2 Test procedure

6.3.2.1 Place sufficient volume of water in the fluid chamber above the soil chamber.

6.3.2.2 Air pressure must be applied gradually to flush water through the sample until no air bubbles in the outflow are observed. For fine-grained soils, the saturation may take several hours to several days, depending on the applied pressure.

6.3.2.3 After the sample is saturated, measure and record the quantity of outflow versus time.

6.3.2.4 Record the pressure reading (h) on the top of the fluid chamber when each reading is made.

6.3.2.5 Plot the accumulated quantity of outflow versus time on rectangular coordinate paper.

6.3.2.6 Stop taking readings as soon as the linear portion of the curve is defined.

6.3.3 Calculations. The hydraulic conductivity can be calculated using the following equation:

$$K = QL/hA \qquad (1)$$

where

K = hydraulic conductivity, LT^{-1}.

L = length of sample, L.

A = cross-sectional area of sample, L^2.

Q = outflow rate, L^3T^1.

h = fluid head difference across the sample, L.

7.0 Triaxial-Cell Method with Back Pressure

7.1 Scope and Application

This method is applicable for all soil types, but especially for fine-grained, compacted, cohesive soils in which full fluid saturation of the sample is difficult to achieve. Normally, the test is run under constant-head conditions.

7.2 Apparatus

The apparatus is similar to conventional triaxial apparatus. The schematic diagram of this apparatus is shown in Figure 5.

7.3 Procedures

7.3.1 Sample preparation. Disturbed or undisturbed samples can be tested. Undisturbed samples must be trimmed to the diameter of the top cap and base of the triaxial cell. Disturbed samples should be prepared in the mold using either kneading compaction for fine-grained soils, or by the pouring and vibrating method for coarse-grained soils, as discussed in Section 4.

7.3.2 Test procedure

7.3.2.1 Measure the dimensions and weight of the prepared sample.

7.3.2.2 Place one of the prepared specimens on the base.

7.3.2.3 Place a rubber membrane in a membrane stretcher, turn both ends of the membrane over the ends of the stretcher, and apply a vacuum to the stretcher. Carefully lower the stretcher and membrane over the specimen as shown in Figure 5. Place the specimen cap on the top of the specimen and release the vacuum on the membrane stretcher. Turn the ends of the membrane down around the base and up around the specimen cap and fasten the ends with O-rings.

7.3.2.4 Assemble the triaxial chamber and place it in position in the loading device. Connect the tube from the pressure reservoir to the base of the triaxial chamber. With valve C (see Figure 5) on the pressure reservoir closed and valves A and B open, increase the pressure inside the reservoir, and allow the pressure fluid to fill the triaxial chamber. Allow a few drops of the pressure fluid to escape through the vent valve (valve B) to insure complete filling of the chamber with fluid. Close valve A and the vent valve.

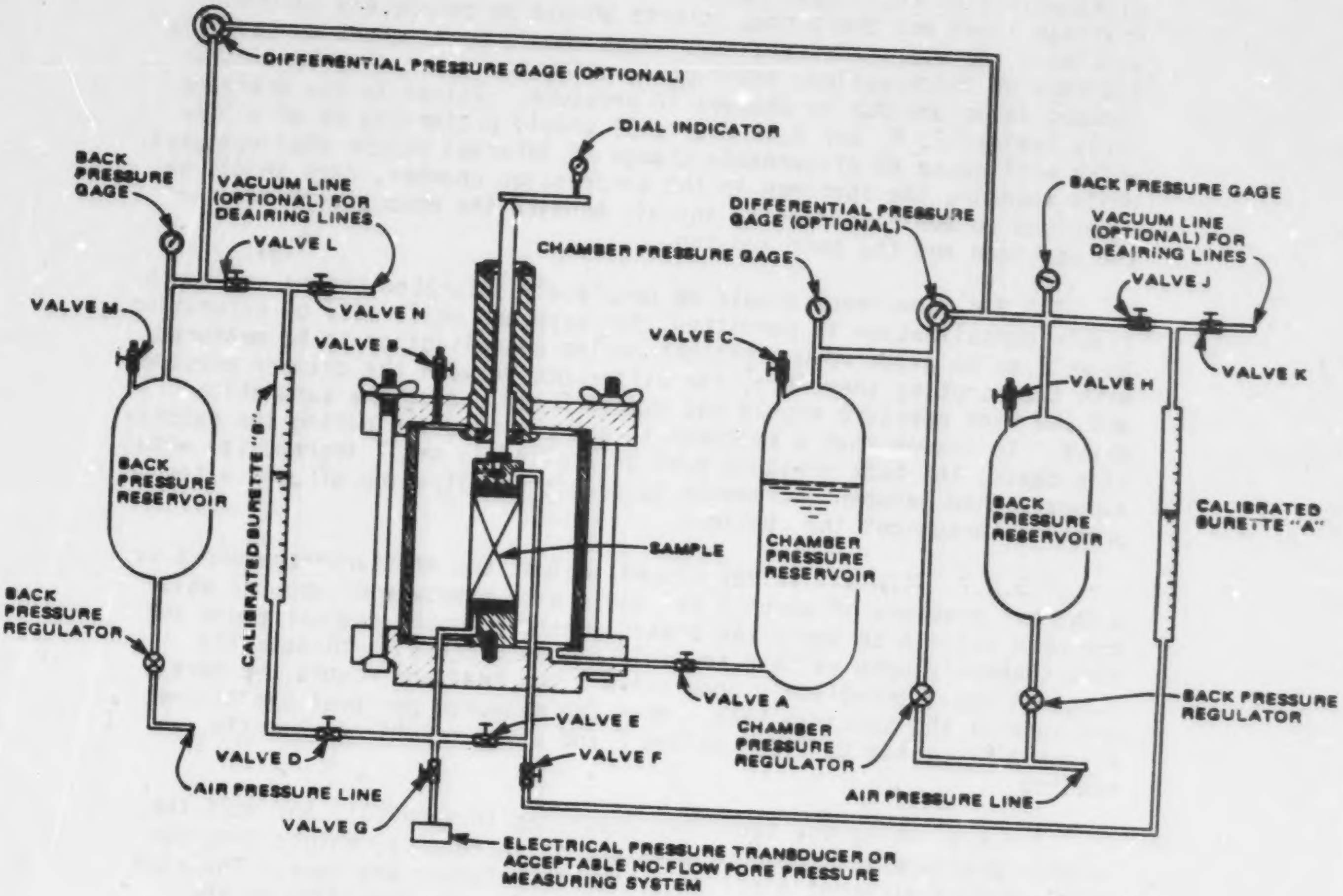

DIFFERENTIAL PRESSURE GAGE (OPTIONAL)
DIAL INDICATOR
BACK PRESSURE GAGE
VACUUM LINE (OPTIONAL) FOR DEAIRING LINES
VALVE L
VALVE M
VALVE N
VALVE B
CHAMBER PRESSURE GAGE
DIFFERENTIAL PRESSURE GAGE (OPTIONAL)
VALVE C
BACK PRESSURE GAGE
VACUUM LINE (OPTIONAL) FOR DEAIRING LINES
VALVE J
VALVE K
VALVE H
BACK PRESSURE RESERVOIR
CALIBRATED BURETTE "B"
SAMPLE
CHAMBER PRESSURE RESERVOIR
BACK PRESSURE RESERVOIR
CALIBRATED BURETTE "A"
BACK PRESSURE REGULATOR
VALVE A
CHAMBER PRESSURE REGULATOR
BACK PRESSURE REGULATOR
VALVE E
VALVE D
VALVE F
AIR PRESSURE LINE
AIR PRESSURE LINE
VALVE G
ELECTRICAL PRESSURE TRANSDUCER OR ACCEPTABLE NO-FLOW PORE PRESSURE MEASURING SYSTEM

FIGURE 5 –– SCHEMATIC DIAGRAM OF TYPICAL TRIAXIAL COMPRESSION APPARATUS FOR HYDRAULIC CONDUCTIVITY TESTS WITH BACK PRESSURE.

SOURCE: U.S. ARMY CORPS OF ENGINEERS, 1970

7.3.2.5 Place saturated filter paper disks having the same diameter as that of the specimen between the specimen and the base and cap; these disks will also facilitate removal of the specimen after the test. The drainage lines and the porous inserts should be completely saturated with de-aired waer. The drainage lines should be as short as possible and made of thick-walled, small-bore tubing to insure minimum elastic changes in volume due to changes in pressure. Valves in the drainage lines (valves E, F, and G in Figure 5) should preferably be of a type which will cause no discernable change of internal volume when operated. While mounting the specimen in the compression chamber, care should be exercised to avoid entrapping any air beneath the membrane or between the specimen and the base and cap.

7.3.2.6 Specimens should be completely saturated before any appreciable consolidation is permitted, for ease and uniformity of saturation, as well as to allow volume changes during consolidation to be measured with the burette; therefore, the difference between the chamber pressure and the back pressure should not exceed 5 psi during the saturation phase. To insure that a specimen is not pre-stressed during the saturation phase, the back pressure must be applied in small increments, with adequate time between increments to permit equalization of pore water pressure throughout the specimen.

7.3.2.7 With all valves closed, adjust the pressure regulators to a chamber pressure of about 7 psi and a back pressure of about 2 psi. Now open valve A to apply the preset pressure to the chamber fluid and simultaneously open valve F to apply the back pressure through the specimen cap. Immediately open valve G and read and record the pore pressure at the specimen base. When the measured por pressure becomes essentially constant, close valves F and G and record the burette reading.

7.3.2.8 Using the technique described in step (3), increase the chamber pressure and the back pressure in increments, maintaining the back pressure at about 5 psi less than the chamber pressure. The size of each increment might be 5, 10, or even 20 psi, depending on the compressibility of the soil specimen and the magnitude of the desired consolidation pressure. Open valve G and measure the pore pressure at the base immediately upon application of each increment of back pressure and observe the pore pressure until it becomes essentially constant. The time required for stabilization of the pore pressure may range from a few minutes to several hours depending on the permeability of the soil. Continue adding increments of chamber pressure and back pressure until, under any increment, the pore pressure reading equals the applied back pressure immediately upon opening valve G.

7.3.2.9 Verify the completeness of saturation by closing valve F and increasing the chamber pressure by about 5 psi. The specimen shall not be considered completely saturated unless the increase in pore pressure immediately equals the increase in chamber pressure.

7.3.2.10 When the specimen is completely saturated, increase the chamber pressure with the drainage valves closed to attain the desired effective consolidation pressure (chamber pressure minus back pressure). At zero elapsed time, open valves E and F.

7.3.2.11 Record time, dial indicator reading, and burette reading at elapsed times of 0, 15, and 30 sec, 1, 2, 4, 8, and 15 min, and 1, 2, 4, and 8 hr, etc. Plot the dial indicator readings and burette readings on an arithmetic scale versus elapsed time on a log scale. When the consolidation curves indicate that primary consolidation is complete, close valves E and F.

7.3.2.12 Apply a pressure to burette B greater than that in burette A. The difference between the pressures in burettes B and A is equal to the head loss (h); h divided by the height of the specimen after consolidation (L) is the hydraulic gradient. The difference between the two pressures should be kept as small as practicable, consistent with the requirement that the rate of flow be large enough to make accurate measurements of the quantity of flow within a reasonable period of time. Because the difference in the two pressures may be very small in comparison to the pressures at the ends of the specimen, and because the head loss must be maintained constant throughout the test, the difference between the pressures within the burettes must be measured accurately; a differential pressure gage is very useful for this purpose. The difference between the elevations of the water within the burettes should also be considered (1 in. of water = 0.036 psi of pressure).

7.3.2.13 Open valves D and F. Record the burette readings at any zero elapsed time. Make readings of burettes A and B and of temperature at various elapsed times (the interval between successive readings depends upon the permeability of the soil and the dimensions of the specimen). Plot arithmetically the change in readings of both burettes versus time. Continue making readings until the two curves become parallel and straight over a sufficient length of time to determine accurately the rate of flow as indicated by the slope of the curves.

7.3.3 Calculations. The hydraulic conductivity can be calculated using the following equation:

$$K = QL/hA \tag{1}$$

where

K = hydraulic conductivity, LT^{-1}.

L = length of sample, L.

A = cross-sectional area of sample, L^2.

Q = outflow rate, L^3T^1.

h = fluid head difference across the sample, L.

8.0 Pressure Chamber Permeameter Method

8.1 Scope and Application

This method can be used to determine hydraulic conductivity of a wide range of soils. Undisturbed and disturbed samples can be tested under falling head conditions using this method. This method is also applicable to both coarse- and fine-grained soils, including remolded, fine-grained materials.

8.2 Apparatus

The apparatus, as shown in Figure 6, consists of

a. Pressure chamber.

b. Standpipe.

c. Specimen cap and base.

d. Coarse porous plates.

The apparatus is capable of applying confining pressure to simulate field stress conditions.

8.3 Procedure

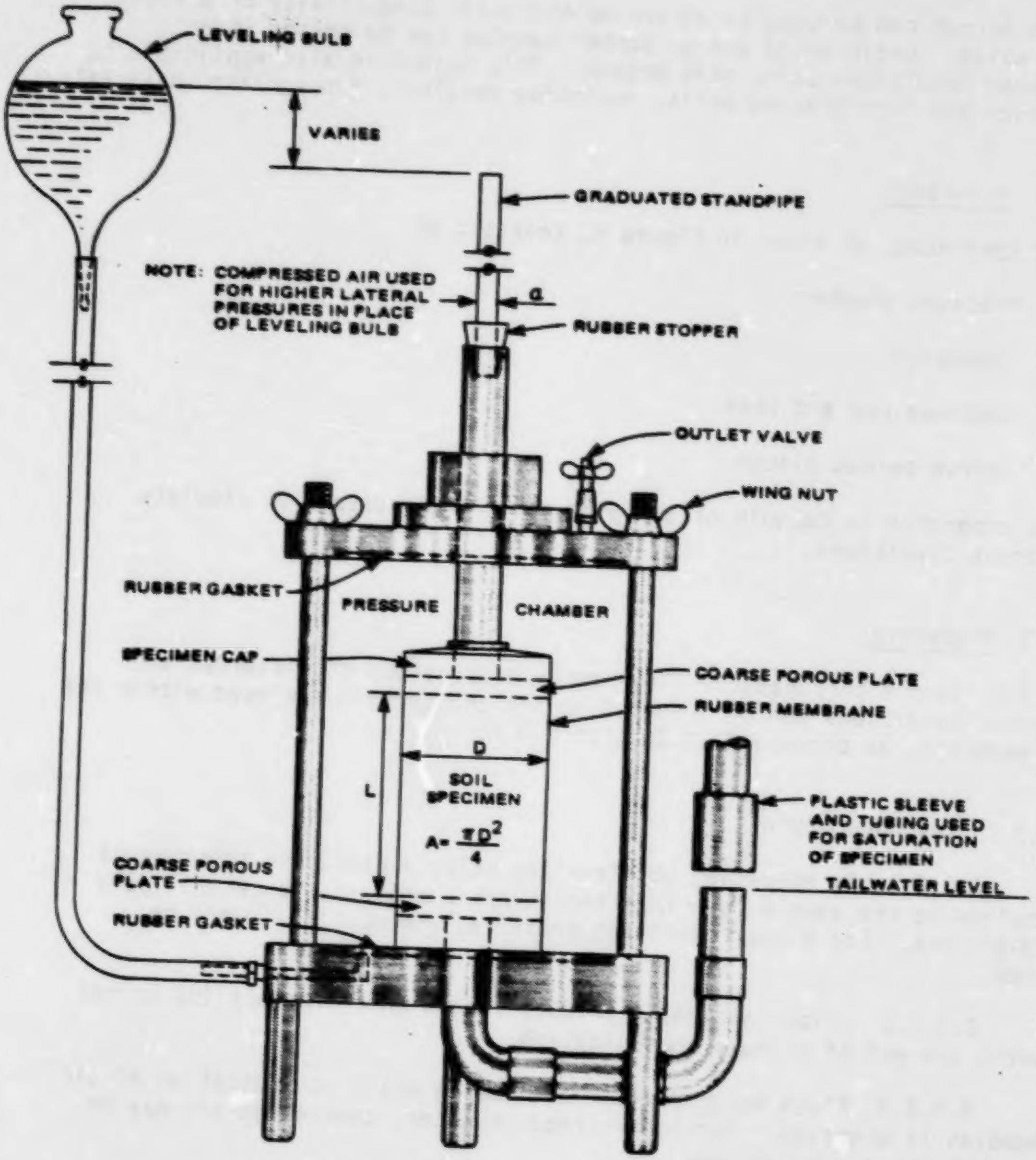
8.3.1 Sample preparation. The sample preparation of disturbed and undisturbed conditions can be prepared in the chamber and enclosed within the rubber membrane, as discussed in Section 7.3.2.

8.3.2 Test procedure

8.3.2.1 By adjusting the leveling bulb, a confining pressure is applied to the sample such that the stress conditions represent field conditions. For higher confining pressure, compressed air may be used.

8.3.2.2 Allow the sample to consolidate under the applied stress until the end of primary consolidation.

8.3.3.3 Flush water through the sample until no indication of air bubbles is observed. For higher head of water, compressed air may be used.


LEVELING BULB
VARIES
GRADUATED STANDPIPE
NOTE: COMPRESSED AIR USED FOR HIGHER LATERAL PRESSURES IN PLACE OF LEVELING BULB
a
RUBBER STOPPER
OUTLET VALVE
WING NUT
RUBBER GASKET
PRESSURE
CHAMBER
SPECIMEN CAP
COARSE POROUS PLATE
RUBBER MEMBRANE
D
L
SOIL SPECIMEN
A= πD²/4
PLASTIC SLEEVE AND TUBING USED FOR SATURATION OF SPECIMEN
COARSE POROUS PLATE
TAILWATER LEVEL
RUBBER GASKET

SOURCE: U.S. ARMY CORPS OF ENGINEERS, 1980

FIGURE 6 PRESSURE CHAMBER FOR HYDRAULIC CONDUCTIVITY

8.3.3.4 Adjust the head of water to attain a desired hydraulic gradient.

8.3.3.5 Measure and record the head drop in the standpipe along with elapsed time until the plot of logarithm of head versus time is linear for more than three consecutive readings.

8.3.3 Calculations. The hydraulic conductivity can be determined using the following equation:

$$k = \frac{2.3\ aL}{At} \log_{10} \frac{h_0}{h_1} \qquad (1)$$

where

a = the cross-sectional area of the standpipe, L^2.

A = the cross-sectional area of the specimen, L^2.

L = the length of the specimen, L.

t = elapsed time from t_1 to t_2, T.

For the setup shown in Figure 2b, the term a/A in the equation is replaced by 1.0. Generally, falling head methods are applicable to fine-grained soils because the testing time is less than constant head methods, and because the low flow rates are more readily observed with the falling head than the constant head methods.

9.0 Leachate Conductivity Using Laboratory Methods

9.1 Scope and Application

9.1.1 Many primary and secondary leachates found at disposal sites may be nonaqueous liquids of aqueous fluids of high ionic strength. These fluids may significantly alter the intrinsic permeability of the porous medium. For example, Anderson and Brown (1981) have demonstrated increases in hydraulic conductivity of compacted clays of as much as two orders of magnitude after the passage of a few pore volumes of a wide range of organic liquids. Consequently, the effects of leachate on these materials should be evaluated by laboratory testing. The preceding laboratory methods can all be used to determine leachate conductivity by using the following guidelines.

The determination of leachate conductivity may be required for both fine-grained and coarse-grained materials. Leachates may either increase or decrease the hydraulic conductivity. Increases are of concern for compacted clay liners, and decreases are of concern for drain materials. The scope and application sections of the preceding methods should be used for selecting an apprropriate test for leachate conductivity. The use of the modified compaction methods (Section 6) for determining leachate conductivity is discussed extensively in EPA publication SW-870 (EPA, 1980).

9.1.2 A supply of leachate must be obtained that is as close in chemical and physical properties to the anticipated leachate at the disposal site as possible. Methods for obtaining such leachate are beyond the scope of this report. However, recent publications by EPA (1980) and Conway and Malloy (1981) give methodologies for simulating the leaching environment to obtain such leachate. Procedures for de-airing the leachate supply are given in Section 2.4. The importance of preventing bacterial growth in leachate tests will depend on the expected conditions at the disposal site. The chemical and physical properties that may result in corrosion, dissolution, or encrustation of laboratory hydraulic conductivity apparatus should be determined prior to conducting a leachate conductivity test. Properties of particular importance are the pH and the vapor pressure of the leachate. Both extremely acidic and basic leachates may corrode materials. In general, apparatus for leachate conductivity tests should be constructed of inert materials, such as acrylic plastic, nylon, or teflon. Metal parts that might come in contact with the leachate should be avoided. Leachates with high vapor pressures may require special treatment. Closed systems for fluid supply and pressure measurement, such as those in the modified triaxial cell methods, should be used.

9.2 Apparatus

In addition to a supply reservoir for water (as shown in Figures 3, 4, 5, and 6) a supply reservoir for leachate is required. Changing the inflow to the test cell from water to leachate can be accomplished by providing a three-way valve in the inflow line that is connected to each of the reservoirs.

9.3 Procedures

The determination of leachate conductivity should be completed immediately following the determination of hydraulic conductivity (Anderson and Brown, 1981). This procedure maintains fluid saturation of the sample, and allows a comparison of the leachate and hydraulic conductivities under the same test conditions. This procedure requires modifications of test operations as described in Section 9.2.

9.3.1 Measurements. Measurements of fluid potential and outflow rates are the same for leachate conductivity and hydraulic conductivity. If the leachate does not alter the intrinsic permeability of the sample, the criteria for the time required to take measurements is the same for leachate conductivity tests as for hydraulic conductivity tests. However, if significant changes occur in the sample by the passage of leachate, measurements should be taken until either the shape of a conductivity versus pore volume curve can be defined, or until the leachate conductivity exceeds the applicable design value for hydraulic conductivity.

9.3.2 Calculations. If the leachate conductivity approaches a constant value, Equations 1 and 2 can be used. If the conductivity changes continuously because of the action of the leachate, the following modifications should be made. For constant head tests, the conductivity should be determined by continuing a plot of outflow volume versus time for the constant rate part of the test conducted with water. For falling head tests, the slope of the logarithm of head versus time should be continued.

If the slope of either curve continues to change after the flow of leachate begins, the leachate is altering the intrinsic permeability of the sample. The leachate conductivity in this case is not a constant. In this case, values of the slope of the outflow curve to use in Equation 1 or 2 must be taken as the tangent to the appropriate outflow curve at the times of measurement. For leachate conductivities that change during the test, a curve of conductivity as a function of pore volumes of leachate should be prepared and reported as part of the test results.

$$K = QL/hA \quad (1)$$

where

K = hydraulic conductivity, LT^{-1}.

L = length of sample, L.

A = cross-sectional area of sample, L^2.

Q = outflow rate, L^3T^1.

h = fluid head difference across the sample, L.

$$K = \frac{2.3\ aL}{At} \log_{10} \frac{h_0}{h_1} \quad (2)$$

where

a = the cross-sectional area of the standpipe, L^2.

A = the cross-sectional area of the specimen, L^2.

L = the length of the specimen, L.

t = elapsed time from t_1 to t_2, T.

For the setup shown in Figure 2b, the term a/A in the equation is replaced by 1.0. Generally, falling head methods are applicable to fine-grained soils because the testing time is less than constant head methods, and because the low flow rates are more readily observed with the falling head than the constant head methods.

10.0 Method for Moderately Permeable Formations Under Confined Conditions

10.1 Scope and Application

This method is applicable for testing zones to which the entire zone is open to the well screen or open bore hole. The method commonly is used in materials of moderate hydraulic conductivity which allow measurement of water-level response over a period of an hour to a few days.

More permeable zones can be tested with rapid response, water level-recording equipment. The method assumes that the tested zone is uniform in all radial directions from the test well. Figure 7 illustrates the test geometry for this method.

10.2 Apparatus

10.2.1 Bailer

10.2.2 Water-level measuring device (e.g., pressure transducer, electric water-level probe, or a steel tape).

10.3 Procedure

10.3.1 The slug test is run by utilizing some method of removing a known volume of water from the well bore in a very short time period and measuring the recovery of the water level in the well. The procedures are the same for both unconfined and confined aquifers. Water is most effectively removed by using a bailer that has been allowed to fill and stand in the well for a sufficiently long period of time so that any water-level disturbance caused by the insertion of the bailer will have reached equilibrium. An alternate method of effecting a sudden change in water level is the withdrawal of a weighted float. The volume of water displaced can be computed using the known submersed volume of the float and Archimedes' principle (Lohman, 1972).

Water-level changes are recorded using either a pressure transducer and a strip-chart recorder, a weighted steel tape, or an electric water-level probe. For testing permeable materials that approach or exceed 70 cm^2/sec, a rapid-response transducer and recorder system is usually used because full recovery may essentially occur in a few minutes. Because the rate of water-level response decays with time, water-level or pressure changes should be taken at increments that are approximately equally spaced in the logarithm of the time since fluid withdrawal. The test should be continued until the water level in the well has recovered to at least 85 percent of the initial pre-test value.

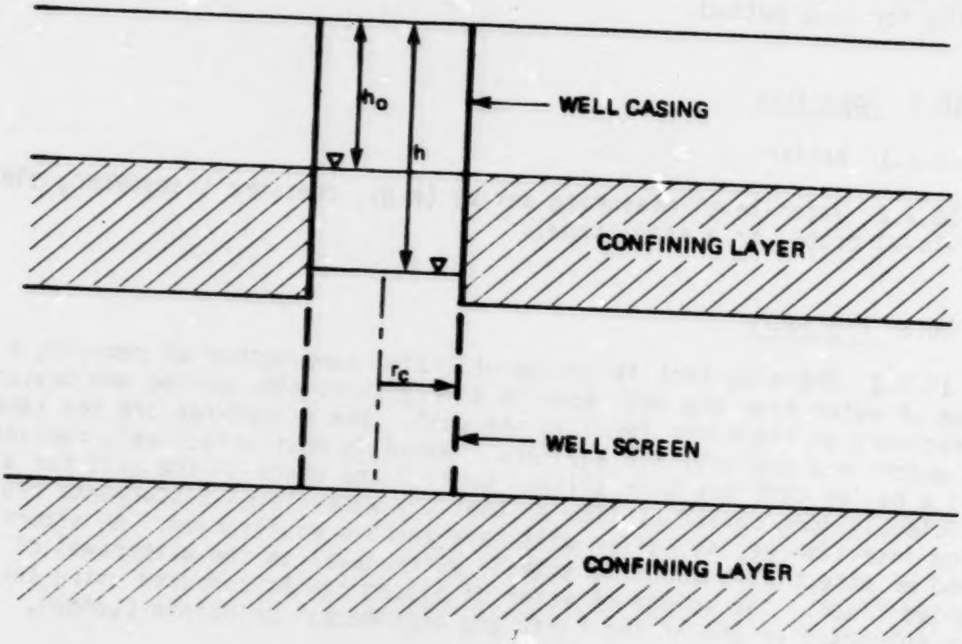

h_o
h
WELL CASING
CONFINING LAYER
r_c
WELL SCREEN
CONFINING LAYER

Figure 7.--Geometry and variable definition for slug tests in confined aquifers.

10.3.2 **Calculations.** Calculations for determining hydraulic conductivity for moderately permeable formations under confined conditions can be made using the following:

10.3.2.1 Determine the transmissivity of the tested zone by plotting the ratio h/h_0 on an arithmetic scale against time since removal of water (t) on a logarithmic scale. The observed fluid potential in the well during the test, as measured by water level or pressure, is h, and h_0 is the fluid potential before the instant of fluid withdrawal. The data plot is superimposed on type curves, such as those given by Lohman (1972), or plotted from Table 3 with the h/h_0 and time axes coincident. The data plot is moved horizontally until the data fits one of the type curves. A value of time on the data plot corresponding to a dimensionless time (β) on the type curve plot is chosen, and the transmissivity is computed from the following:

$$T = \frac{\beta r_c^2}{t}$$

where r_c is the radius of the casing (Lohman, 1972, p. 29).

The type curves plotted using data in Table 3 are not to be confused with those commonly referred to as "Theis Curves," which are used for pumping tests in confined aquifers (Lohman, 1972). The type curve method is a general technique of determining aquifer parameters when the solution to the descriptive flow equation involves more than one unknown parameter. Although both the storage coefficient and transmissivity of the tested interval can be determined with the type curve method for slug tests, determination of storage coefficients is beyond the scope of this report. See Section 10.3.3 for further discussion of the storage coefficient.

If the data in Table 3 are used, a type curve for each value of α is prepared by plotting $F(\alpha,\beta)$ on the arithmetic scale and dimensionless time (β) on the logarithmic scale of semilog paper.

10.3.2.2 Determine the hydraulic conductivity by dividing the transmissivity by the thickness of the tested zone.

10.3.3 Sources of error. The errors that can arise in conducting slug tests can be of three types: those resulting from the well or bore hole construction, measurement errors, and data analysis errors.

TABLE 3. VALUES OF THE FUNCTION F(α,β), FOR USE IN THE CONVENTIONAL AND PRESSURIZED SLUG TESTS. SOURCE: PAPADOPULOS ET.AL. (1973).

Tt/r_c^2	$\alpha = 10^{-6}$	$\alpha = 10^{-7}$	$\alpha = 10^{-8}$	$\alpha = 10^{-9}$	$\alpha = 10^{-10}$
0.001	0.9994	0.9996	0.9996	0.9997	0.9997
0.002	0.9989	0.9992	0.9993	0.9994	0.9995
0.004	0.9980	0.9985	0.9987	0.9989	0.9991
0.006	0.9972	0.9978	0.9982	0.9984	0.9986
0.008	0.9964	0.9971	0.9976	0.9980	0.9982
0.01	0.9956	0.9965	0.9971	0.9975	0.9978
0.02	0.9919	0.9934	0.9944	0.9952	0.9958
0.04	0.9848	0.9875	0.9894	0.9908	0.9919
0.06	0.9782	0.9819	0.9846	0.9866	0.9881
0.08	0.9718	0.9765	0.9799	0.9824	0.9844
0.1	0.9655	0.9712	0.9753	0.9784	0.9807
0.2	0.9361	0.9459	0.9532	0.9587	0.9631
0.4	0.8828	0.8995	0.9122	0.9220	0.9298
0.6	0.8345	0.8569	0.8741	0.8875	0.8984
0.8	0.7901	0.8173	0.8383	0.8550	0.8686
1.0	0.7489	0.7801	0.8045	0.8240	0.8401
2.0	0.5800	0.6235	0.6591	0.6889	0.7139
3.0	0.4554	0.5033	0.5442	0.5792	0.6096
4.0	0.3613	0.4093	0.4517	0.4891	0.5222
5.0	0.2893	0.3351	0.3768	0.4146	0.4487
6.0	0.2337	0.2759	0.3157	0.3525	0.3865
7.0	0.1903	0.2285	0.2655	0.3007	0.3337
8.0	0.1562	0.1903	0.2243	0.2573	0.2888
9.0	0.1292	0.1594	0.1902	0.2208	0.2505
10.0	0.1078	0.1343	0.1620	0.1900	0.2178
20.0	0.02720	0.03343	0.04129	0.05071	0.06149
30.0	0.01286	0.01448	0.01667	0.01956	0.02320
40.0	0.008337	0.008898	0.009637	0.01062	0.01190
50.0	0.006209	0.006470	0.006789	0.007192	0.007709
60.0	0.004961	0.005111	0.005283	0.005487	0.005735
80.0	0.003547	0.003617	0.003691	0.003773	0.003863
100.0	0.002763	0.002803	0.002845	0.002890	0.002938
200.0	0.001313	0.001322	0.001330	0.001339	0.001348

TABLE 3. Continued. EXTENDED VALUES OF F(α,β), FOR USE IN SLUG TESTS. SOURCE: BREDEHOEFT AND PAPADOPULOS (1980).

β	α=0.1	α=0.2	α=0.5	α=1	α=2	α=5	α=10
0.000001	0.9993	0.9990	0.9984	0.9977	0.9968	0.9948	0.9923
0.000002	0.9990	0.9986	0.9977	0.9968	0.9955	0.9927	0.9894
0.000004	0.9986	0.9980	0.9968	0.9955	0.9936	0.9898	0.9853
0.000006	0.9982	0.9975	0.9961	0.9945	0.9922	0.9876	0.9822
0.000008	0.9980	0.9971	0.9955	0.9936	0.9910	0.9857	0.9796
0.00001	0.9977	0.9966	0.9949	0.9929	0.9900	0.9841	0.9773
0.00002	0.9968	0.9955	0.9929	0.9900	0.9858	0.9776	0.9683
0.00004	0.9955	0.9936	0.9899	0.9858	0.9801	0.9687	0.9558
0.00006	0.9944	0.9922	0.9877	0.9827	0.9757	0.9619	0.9464
0.00008	0.9936	0.9909	0.9858	0.9800	0.9720	0.9562	0.9387
0.0001	0.9929	0.9859	0.9841	0.9777	0.9688	0.9512	0.9318
0.0002	0.9898	0.9857	0.9776	0.9687	0.9562	0.9321	0.9059
0.0004	0.9855	0.9797	0.9685	0.9560	0.9385	0.9061	0.8711
0.0006	0.9822	0.9752	0.9615	0.9465	0.9258	0.8869	0.8458
0.0008	0.9794	0.9713	0.9557	0.9385	0.9151	0.8711	0.8253
0.001	0.9769	0.9679	0.9505	0.9315	0.9057	0.8576	0.8079
0.002	0.9670	0.9546	0.9307	0.9048	0.8702	0.8075	0.7450
0.004	0.9528	0.9357	0.9031	0.8686	0.8232	0.7439	0.6684
0.006	0.9417	0.9211	0.8825	0.8419	0.7896	0.7001	0.6178
0.008	0.9322	0.9089	0.8654	0.8202	0.7626	0.6662	0.5797
0.01	0.9238	0.8982	0.8505	0.8017	0.7400	0.6384	0.5492
0.02	0.8904	0.8562	0.7947	0.7336	0.6595	0.5450	0.4517
0.04	0.8421	0.7980	0.7214	0.6489	0.5854	0.4454	0.3556
0.06	0.8048	0.7546	0.6697	0.5919	0.5055	0.3872	0.3030
0.08	0.7734	0.7150	0.6289	0.5486	0.4618	0.3469	0.2682
0.1	0.7459	0.6885	0.5951	0.5137	0.4276	0.3168	0.2428
0.2	0.6418	0.5774	0.4799	0.4010	0.3234	0.2313	0.1740
0.4	0.5095	0.4458	0.3566	0.2902	0.2292	0.1612	0.1207
0.6	0.4227	0.3642	0.2864	0.2311	0.1817	0.1280	0.09616
0.8	0.3598	0.3072	0.2397	0.1931	0.1521	0.1077	0.08134
1.	0.3117	0.2648	0.2061	0.1663	0.1315	0.09375	0.07120
2.	0.1786	0.1519	0.1202	0.09912	0.08044	0.05940	0.04620
4.	0.08761	0.07698	0.06420	0.05521	0.04668	0.03621	0.02908
6.	0.05527	0.04599	0.04331	0.03830	0.03324	0.02663	0.02185
8.	0.03963	0.03658	0.03254	0.02933	0.02594	0.02125	0.01771
10.	0.03065	0.02870	0.02600	0.02376	0.02130	0.01776	0.01499
20.	0.01408	0.01361	0.01288	0.01219	0.01133	0.009943	0.008716
40.	0.006680	0.006568	0.006374	0.006171	0.005897	0.005395	0.004898
60.	0.004367	0.004318	0.004229	0.004132	0.003994	0.003726	0.003445
80.	0.003242	0.003214	0.003163	0.003105	0.003022	0.002853	0.002668
100.	0.002577	0.002559	0.002526	0.002487	0.002431	0.002313	0.002181
200.	0.001271	0.001264	0.001258	0.001247	0.001230	0.001194	0.001149
400.	0.0006307	0.0006295	0.0006272	0.0006242	0.0006195	0.0006085	0.0005944
600.	0.0004193	0.0004188	0.0004177	0.0004163	0.0004141	0.0004087	0.0004016
800.	0.0003148	0.0003137	0.0003131	0.0003122	0.0003110	0.0003078	0.00030[illegible]5
1000.	0.0002510	0.0002508	0.0002504	0.0002495	0.0002490	0.0002469	0.0002440

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10.3.3.1 Well construction and development errors. This method assumes that the entire thickness of the zone of interest is open to the well screen or bore holes and that flow is principally radial. If this is not the case, the computed hydraulic conductivity may be too high. If the well is not properly developed, the computed conductivity will be too low.

10.3.3.2 Measurement errors can result from determining or recording the fluid level in the bore hole and the time of measurement incorrectly. Water levels should be measured to an accuracy of at least 1 percent of the initial water-level change. For moderately permeable materials, time should be measured with an accuracy of fractions of minutes, and for more permeable materials, the time should be measured in terms of seconds or fractions of seconds. The latter may require the use of a rapid-response, pressure transducer, and recorder system.

10.3.3.3 Data analysis errors. The type curve procedure requires matching the data to one of a family of type curves, described by the parameter α, which is a measure of the storage in the well bore and aquifer. Papadopulos and others (1973) show that an error of two orders of magnitude in the selection of α could result in an error of less than 30 percent in the value of transmissivity determined. Assuming no error in determining the thickness of the zone tested, this is equivalent to a 30% error in the hydraulic conductivity.

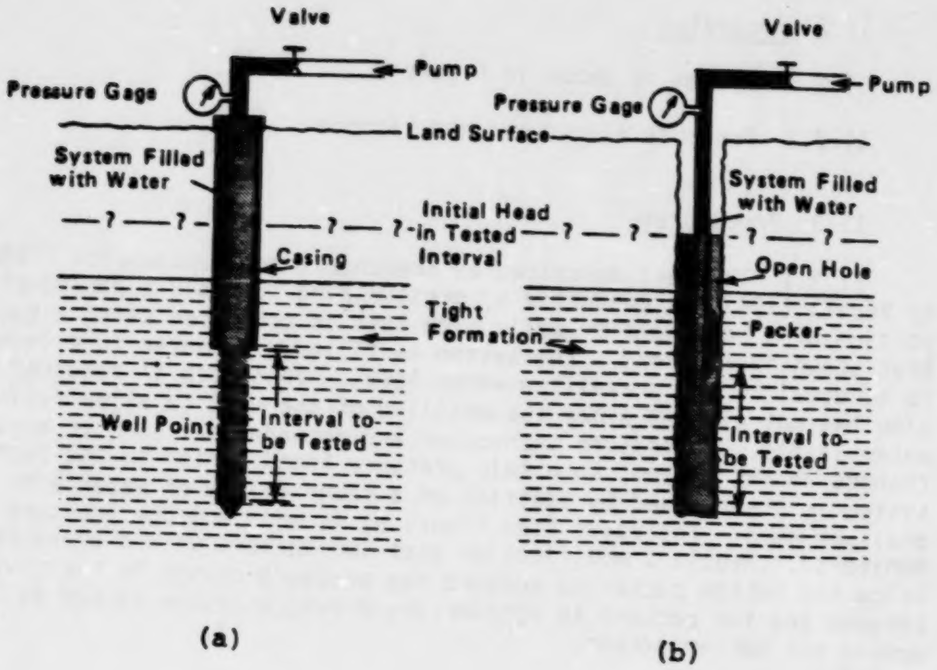

Valve
Pump
Pressure Gage
Land Surface
System Filled with Water
Initial Head in Tested Interval
Casing
Tight Formation
Well Point
Interval to be Tested
(a)
Valve
Pump
Pressure Gage
System Filled with Water
Open Hole
Packer
Interval to be Tested
(b)

Figure 8.--Schematic diagram for pressurized slug test method in unconsolidated (a) and consolidated (b) materials. Source: Papadopulos and Bredehoeft, 1980.

11.0 Methods for Extremely Tight Formations Under Confined Conditions

11.1 Scope and Application

This test is applicable to materials that have low to extremely low permeability such as silts, clays, shales, and indurated lithologic units. The test has been used to determine hydraulic conductivities of shales of as low as 10^{-10} cm/sec.

11.2 Apparatus

11.2.1 System as shown in Figure 8.

11.2.2 Pressure transducer and recorder.

11.3 Procedures

11.3.1 The test described by Bredehoeft and Papadopulos (1980) and modified by Neuzil (1982) is conducted by pressurizing suddenly a packed-off zone in a portion of a bore hole or well. The test is conducted using a system such as that shown in Figure 8. The system is filled with water to a level assumed to be equal to the prevailing water level. This step is required if sufficient time has not elapsed since the drilling of the well to allow full recovery of water levels. A pressure transducer and recorder are used to monitor pressure changes in the system, to obtain pressure trends prior to the test. The system is pressurized by addition of a known volume of water with a high pressure pump. The valve (see Figure 8) is shut and the pressure decay is monitored. Neuzil's modification uses two packers with a pressure transducer below the bottom packer to measure the pressure change in the cavity and one between the two packers to monitor any pressure change caused by leakage around the bottom packer.

11.3.2 Calculations. The modified slug test, as developed by Bredehoeft and Papadopulos (1980), considered compressive storage of water in the bore hole. These authors considered that the volume of the packed-off bore hole did not change during the test and that all compressive storage resulted in compression of water under the pressure pulse. Neuzil (1980) demonstrated that under some test conditions this is not a valid assumption. The computational procedure is the same in either case. Data are plotted in the same manner as for the conventional slug test, and type curves are used from either Lohman (1972), or plotted from data given in Table 3, as described in Sections 3.2. The value of time (t) and dimensionless time, ( ), are determined in the same manner as for the conventional tests. If the compression of water only is considered, transmissivity is computed by replacing r_c^2 by the quantity $(V_w\ C_w \rho\ g/\pi)$ in Equation 1:

$$T = \frac{\beta(V_w\ C_w\ \rho_g/\pi)^2}{t}$$

where

V_w is the volume of water in the packed off cavity, L^3.

C_w is the compressibility of water, LT^2M^{-1}.

ρ is the density of water ML^{-3}.

g is the acceleration of gravity, LT^{-2}.

If the compressive storage is altered by changing the volume of the packed-off cavity (V), then the combined compressibilty of the water and the expansion of the cavity (C_o) is used in the equation instead of C_w. C_o is computed by measuring the volume of water injected during pressurization (ΔV) adn the pressure change ΔP for the pressurization:

$$C_o = \frac{\Delta V}{V \Delta P}$$

(Neuzil, 1982, page 440). Use of C_o requires an accurate method of metering the volume of water injected and the volume of the cavity.

11.3.3 Sources of Error. The types of errors in this method are the same as those for the conventional slug test. Errors may also arise by inaccurate determination of the cavity volume and volume of water injected. An additional assumption that is required for this method is that the hydraulic properties of the interval tested remain constant throughout the test. This assumption can best be satisfied by limiting the initial pressure change to a value only sufficiently large enough to be measured (Bredehoeft and Papadopulos, 1980).

12.0 Methods for Moderately Permeable Materials Under Unconfined Conditions

12.1 Scope and Application

This method is applicable to wells that fully or partially penetrate the interval of interest (Figure 9). The hydraulic conductivity determined will be principally the value in the horizontal direction (Bouwer and Rice, 1976).

12.2 Apparatus

12.2.1 Bailer or submerged float.

12.2.2 Pressure transducer and recorder on a wetted steel tape or an electric water-level sounder.

12.3 Procedures

12.3.1 A general method was developed by Bouwer and Rice (1976) for testing cased wells that partly or fully penetrate aquifers that have a water table as the upper boundary of the zone to be tested. The geometry and dimensions that are required to be known for the method are shown in Figure 1. The test is accomplished by effecting a sudden change in fluid potential in the well by withdrawal of either a bailer or submersed float, as discussed in Section 10.3.1. Water-level changes can be monitored with either a pressure transducer and recorder, a wetted steel tape, or an electric water-level sounder. For higher permeable formations, a rapid-response transducer and recorder system is required. The resolution of the transducer should be about 0.01 m.

12.3.2 Calculations. The hydraulic conductivity is calculated using the following equation in the notation of this report, taken from Bouwer and Rice (1976):

$$K = \frac{r_c^2 \ln \bar{R}/r_w}{2 L_e t} \ln \frac{Y_0}{Y} \qquad (1)$$

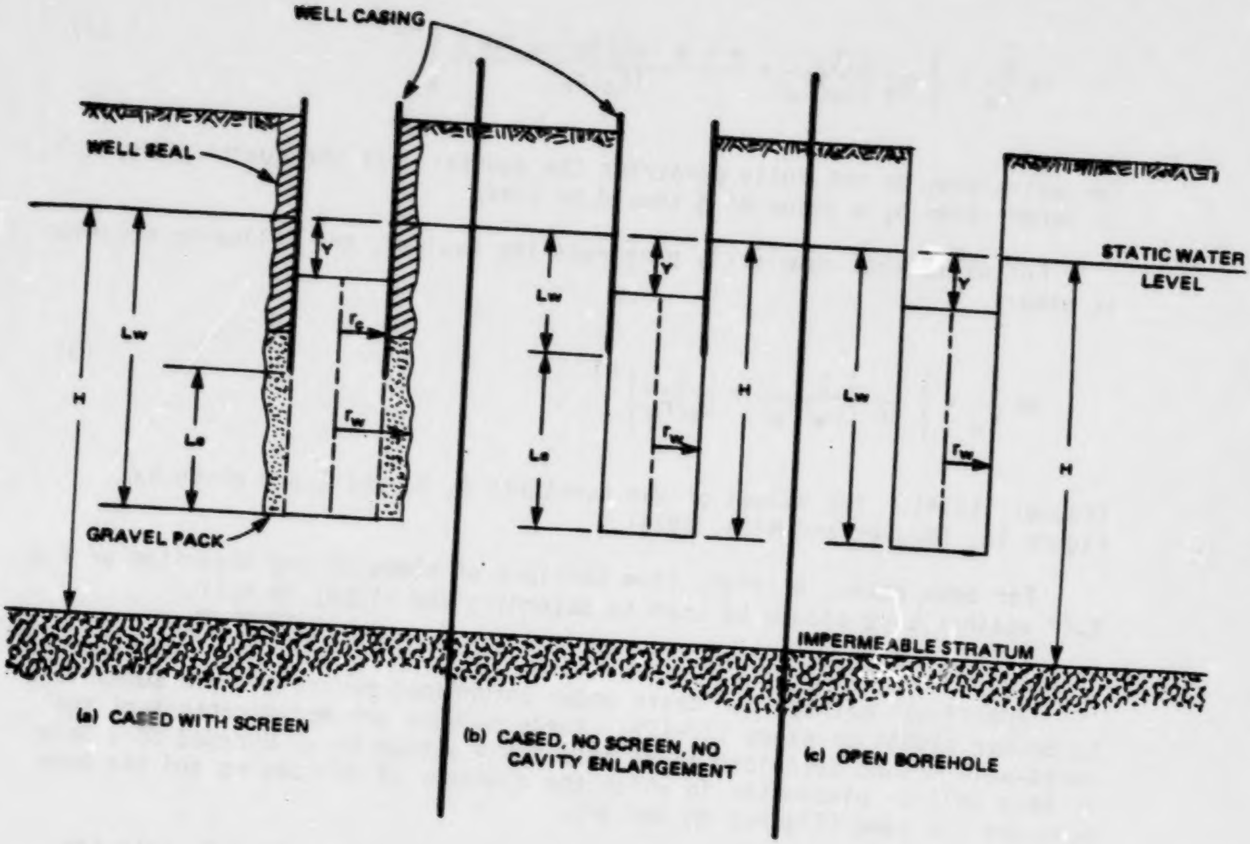

WELL CASING
WELL SEAL
Y
Lw
r_c
H
Le
r_w
GRAVEL PACK
STATIC WATER LEVEL
IMPERMEABLE STRATUM
(a) CASED WITH SCREEN
(b) CASED, NO SCREEN, NO CAVITY ENLARGEMENT
(c) OPEN BOREHOLE

Figure 9.--Variable definitions for slug tests in unconfined materials. Cased wells are open at the bottom.

where r_c, r_w, L_e, t, Y, and K have been previously defined or are defined in Figure 8.1. Y_o is the value of Y immediately after withdrawal of the slug of water. The term R is an effective radius that is computed using the following equation given by Bouwer and Rice (1976):

$$\ln \frac{\bar{R}}{r_w} = \left\{ \frac{1.1}{\ln (L_w/r_w)} + \frac{A + B \ln[(H_o - L_w)/r_w]}{(L_e/r_w)} \right\}^{-1} \qquad (2)$$

for wells that do not fully penetrate the aquifer. If the quantity $(H_o - L_w/r_w)$ is larger than 6, a value of 6 should be used.

For wells that completely penetrate the aquifer, the following equation is used:

$$\ln \frac{\bar{R}}{r_w} = \left\{ \frac{1.1}{\ln (L_w/r_w)} + \frac{C}{L_e/r_w} \right\}^{-1} \qquad (3)$$

(Bouwer, 1976). The values of the constants A, B, and C are given by Figure 10, (Bouwer and Rice, 1976).

For both cases, straight line portions of plots of the logarithm of Y or Y_o/Y against time should be used to determine the slope, $\frac{\ln Y_o/Y}{t}$.

Additional methods for tests under unconfined conditions are summarized by Bouwer (1966) on pages 117-122. These methods are modifications of the cased-well method described above that apply either to an uncased bore hole or to a well or piezometer in which the diameter of the casing and the bore hole are the same (Figures 9b and 9c).

Van de Kamp (1976) has also developed a methodology to calculate the transmissivity of highly permeable aquifers. This is achieved by an analysis of slug test results in which the problem of an under-dampened well response is considered. Such a response may occur in a highly permeable aquifer because the inertia of water in the well column results in force-free oscillations in the water level in the well. However, a high degree of interpretation is associated with this methodology, comparable to the analysis required for pump tests. It is also appropriate primarily for situations where the wells and tested zones are in the shallow sub-surface.

12.3.3 Sources of error. The method assumes that flow of water from above is negligible. If this assumption cannot be met, the conductivities may be in error. Sufficient flow from the unsaturated zone by drainage would result in a high conductivity value. Errors caused by measuring water levels and recording time are similar to those discussed in Sections 10.3.3 and 11.3.3.

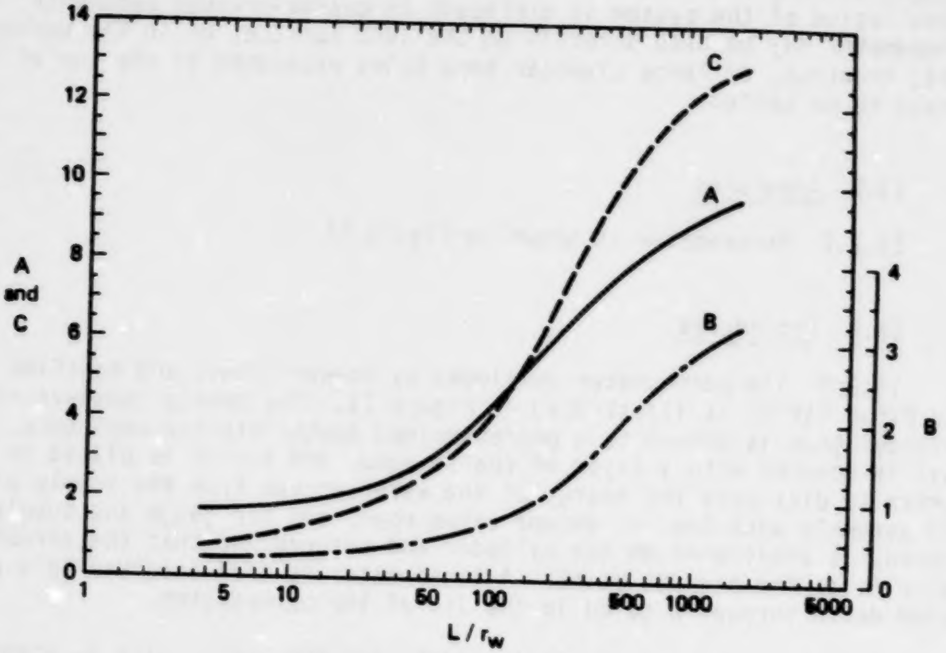


FIGURE 10.-- CURVES DEFINING COEFFICIENTS A, B, AND C IN EQUATIONS 13 and 14 AS A FUNCTION OF THE RATIO L / r_W

SOURCE : BOWER AND RICE , 1976.

13.0 Air Entry Permeameter

13.1 Scope and Application

The air entry permeameter provides a simple and rapid field method for measuring vertical hydraulic conductivity in the absence of a water table. This approach enables an in-situ analysis of larger samples than is common with laboratory tests and can, thus, incorporate the effects of secondary porosity characteristics, such as of worm or root holes and cracks. The method is most applicable for the investigation of dry, fine-grained sediments. The test is not well suited to the study of initially wet soils because the induced wetting front remains indistinct, hindering the analysis, and the installation of the system is difficult in coarse-grained sediments. The permeameter may be used directly on the land surface, or in the bottom of pits, trenches, or large diameter bore holes excavated to the top of the strata to be tested.

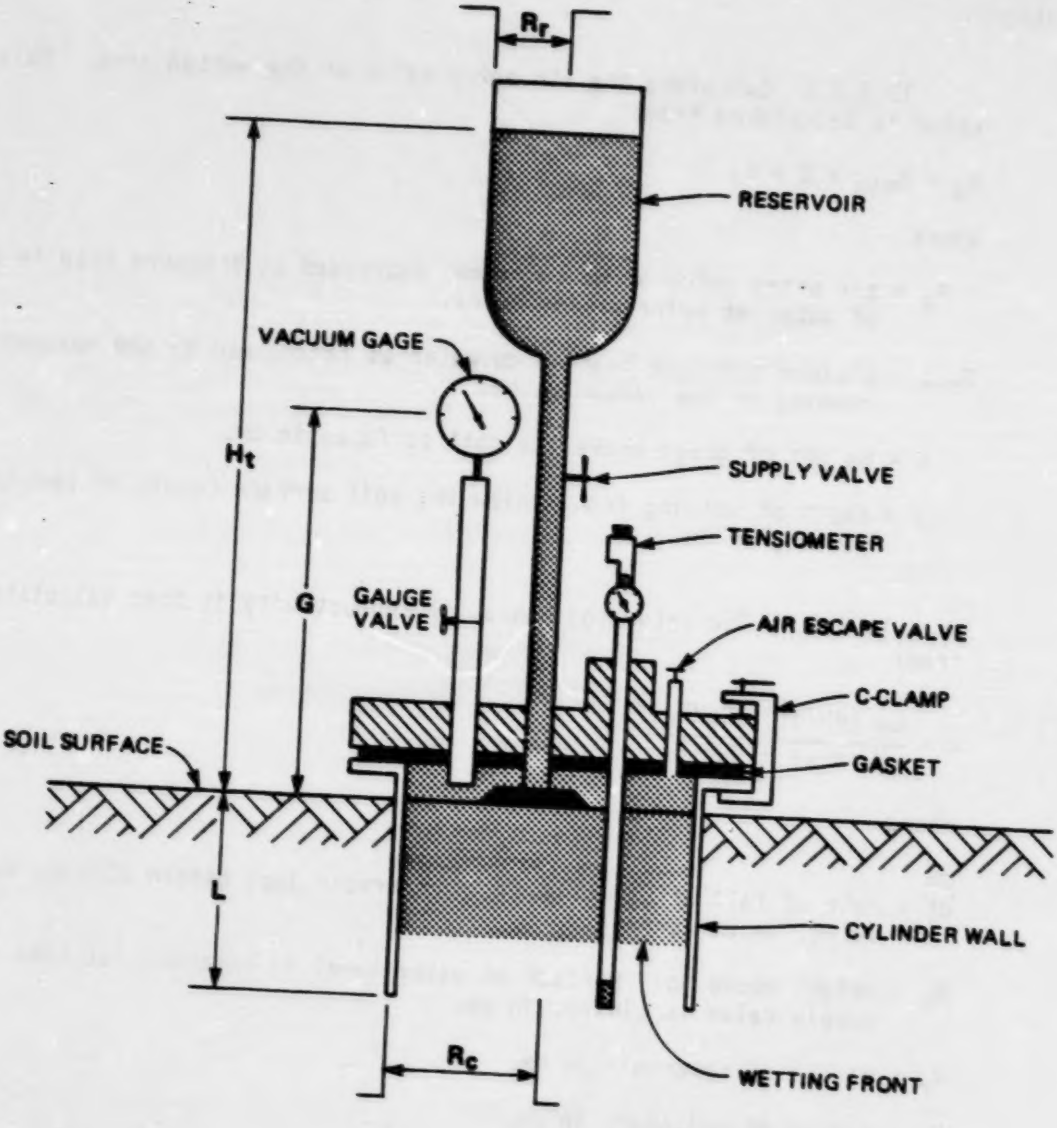
13.2 Apparatus

13.2.1 Permeameter as shown in Figure 11.

13.3 Procedures

13.3.1 The permeameter developed by Bouwer (1966) and modified by Topp and Binns (1976) is illustrated in Figure 11. The device consists of a metal cylinder that is driven to a predetermined depth into the sediments. The soil is covered with a layer of coarse sand, and a disk is placed in the center to dissipate the energy of the water stream from the supply pipe. The lid assembly with the air escape valve open, and the gauge and supply valves closed, is positioned on the cylinder and secured, so that the air-escape valve is at the highest point. A tensiometer is then inserted to a predetermined depth through a guide in the lid of the permeameter.

The water reservoir is filled next, and the supply line is opened to quickly fill the apparatus, while air is allowed to escape through the air valve. Once the apparatus is filled with water, and all air is removed, the air escape valve is closed. Immediately after the air valve is closed, the measurement of the rate of flow of water from the reservoir is initiated and continued until the wetting front causes the tensiometer reading to decrease toward zero. When a vacuum gauge tensiometer is used, the zero soil moisture suction may be simply read from the dial. However, if a manometer scale is used, this must be calibrated using the techniques outlined by Black (1965) and Curtis and Trudgill (1974), before a reading can be obtained. The water supply valve is then closed, and the air entry pressure is determined as the maximum vacuum observed on the vacuum gauge, while drainage occurs from within the permeameter.


R_r
RESERVOIR
H_t
VACUUM GAGE
G
SUPPLY VALVE
TENSIOMETER
GAUGE VALVE
AIR ESCAPE VALVE
C-CLAMP
SOIL SURFACE
GASKET
L
CYLINDER WALL
R_c
WETTING FRONT

SOURCE: TOPP AND BINNS (1976)

FIGURE 11 MODIFIED AIR ENTRY PERMEAMETER

13.3.2 Calculations. The calculations to determine the saturated hydraulic conductivity using the air entry permeameter are made in two stages.

13.3.2.1 Calculate the air entry value of the wetted zone. This value is calculated from:

$$P_a = P_{min} + G + L_f$$

where

P_a = air entry value of wetted zone, expressed as pressure head in cm of water at point of air entry.

P_{min} = minimum pressure head in cm water as determined by the maximum reading on the vacuum gauge.

G = height of gauge above the soil surface, in cm.

L_f = depth of wetting front below the soil surface (depth of tensiometer), in cm.

13.3.2.2 The saturated hydraulic conductivity is then calculated from:

$$K = \frac{L_f \, (dH/dt) \, (R_r/R_c)^2}{H_r + L_f - 0.5 \, P_a}$$

where

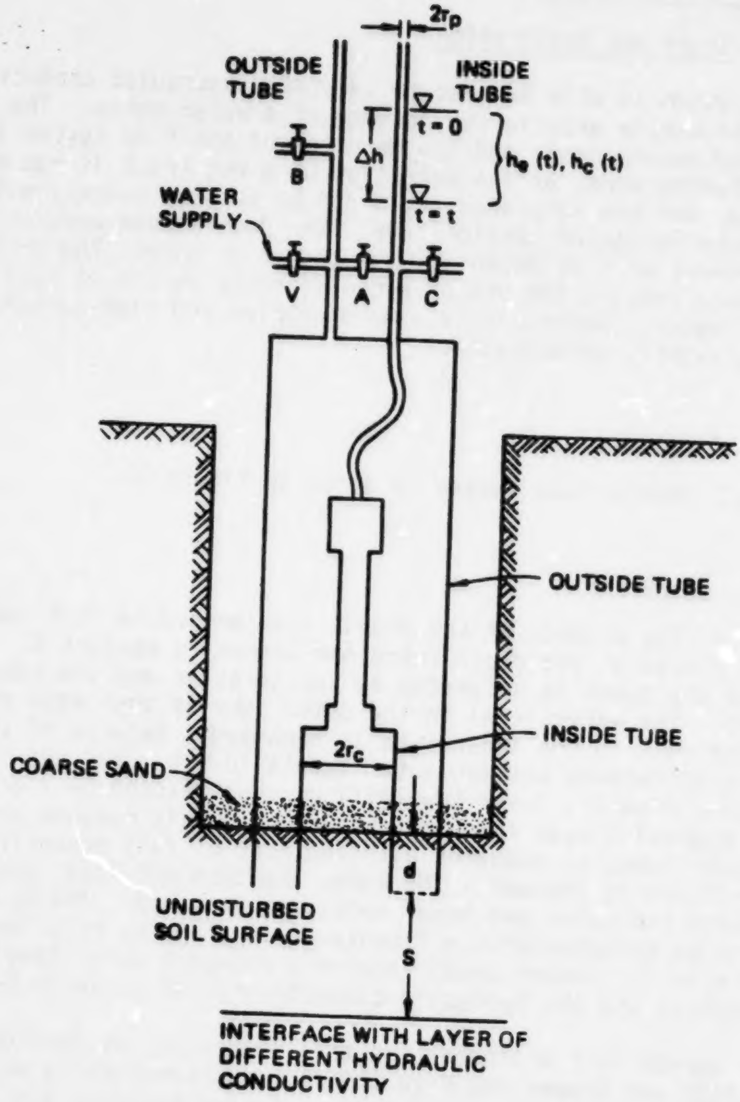
$\frac{dH}{dt}$ = rate of fall of water level in reservoir just before closing supply valve, in cm sec^{-1}.

H_r = height above soil surface of water level in reservoir at time supply valve is closed, in cm.

R_r = radius of reservoir in cm.

R_c = radius of cylinder, in cm.

13.3.3 Sources of error. Potential sources of error in this approach include leakage at the edge of the cylinder because of a poor bond between the apparatus and the soil and the compaction or disturbance of the soil during installation (a particular problem in coarse-grained sediments). If the soil is not dry prior to the test, error may be introduced into the calculations because of the indistinctness of the wetting front.


2rp
OUTSIDE TUBE
INSIDE TUBE
t = 0
Δh
he (t), hc (t)
B
t = t
WATER SUPPLY
V
A
C
OUTSIDE TUBE
INSIDE TUBE
2rc
COARSE SAND
d
UNDISTURBED SOIL SURFACE
S
INTERFACE WITH LAYER OF DIFFERENT HYDRAULIC CONDUCTIVITY

SOURCE: BOUWER AND RICE (1967)

FIGURE 12 EQUIPMENT FOR THE DOUBLE TUBE METHOD

14.0 Double Tube Method

14.1 Scope and Application

This system is able to measure saturated hydraulic conductivity in a well-defined sample area in the absence of a water table. The method is free of simplying assumptions, and the geometry of the flow system is taken into account. Furthermore, as the detection of a wet front is not required in this method, wet and saturated soils can be studied readily without the need for the installation of tensiometers. The double tube apparatus also enables the measurement of K at depths of 0.2 to 3 m or more. The methodology, however, does require the use of a considerable amount of equipment and large volumes of water. Hence, it is a more complex and time-consuming approach than the air-entry permeameter.

14.2 Apparatus

14.2.1 Double tube system is shown in Figure 12.

14.3 Procedure

14.3.1 The essence of the double tube method is that two concentric tubes are placed at the depth where one wishes to measure K. The soil below and around the tubes is saturated by infiltration and the tubes are filled with water. The water level in the outer tube is then kept constant, while the rate of fall in the inner tube is recorded. Because of the gradually increasing difference between water levels in the outer and inner tubes, the infiltration from the inner tube will be counteracted by a gradually increasing hydraulic head from the outer tube. This reduces the rate of fall of the inner tube, as compared with the rate of fall occurring when the equal level condition is imposed. The tubes are then refilled, and the rates of fall in both the outer and inner tubes are measured. The hydraulic conductivity can be computed with a formula expressing the relation between the difference in fall under equal level and constant outer level conditions, the flow geometry, and the hydraulic conductivity, as given in Section 14.3.2.

The appropriate equipment for this technique, as developed by Bouwer (1961, 1962) and Bouwer and Rice (1967), is schematically described in Figure 1. It consists of a water reservoir connected by pipes and valves to the inner and outer tubes in such a way that the conditions of equal level fall and constant outer level can be imposed. A large auger and cleaning equipment are also required to return the disturbed structure of the bottom of the hole to its original conditions (Black, 1965).

To enable the measurement of K, a hole must first be augered to the desired depth and then cleaned to produce an undisturbed surface at the base. A 1 cm layer of coarse, dry sand is placed over the cleaned surface. The outside tube is then placed in the hole and forced through the sand to the original surface. A disk should be placed over the surface to dissipate the energy of the water stream that will fill the tube. The outside tube is then filled with water and the energy breaker removed while the water level is maintained. The outside tube is forced down about 5 cm to obtain a seal, so that water does not rise on the outside of the tube.

After the soil has come close to saturation (after about 1 hour for fine-grained soils, less for coarse-grained soils), the inner tube is lowered inside the outer tube and forced down until it penetrates the soil surface. The depth of penetration should be about 2 cm in fine-grained soils and 3 cm in coarser soil. One end of the flexible tubing is then connected to the inside tube.

Both tubes are filled simultaneously, to avoid excessive pressure differences between the two tubes. The top plate is held above the hole, with the water supply temporarily connected to inlet C (Figure 12) on the inner tube standpipe, with valve A open, and valves B and V closed. With water flowing from both standpipes, the upper end of the flexible tubing is connected to the inner tube standpipe, and the top plate is bolted to the outer tube. When the outer tube standpipe overflows, the water supply is changed from C to V with valve A still open. The flow rate should then be adjusted so that the water level in the inner tube standpipe is maintained at the zero mark and the outer tube standpipe is overflowing slightly.

14.3.1.1 To enable the calculation of K, two sets of readings are necessary.

14.3.1.1.1 Constant outer level conditions. Close valve A while the water level in the outer tube is maintained to overflowing. The time required for the water level in the inner tube standpipe to drop through increments of 5 cm (or some other preselected distance) to a total of 30 cm should be recorded. Then add water to the inner tube standpipe immediately to restore the water level to the zero mark, and open valve A to return to the initial equilibrium condition.

14.3.1.1.2 Equal level conditions. To make the second measurements, start the stop watch at the time valves A and V are closed, and manipulate valve B so that the rate of fall of the water level in the outer tube standpipe is equal to that in the inner tube standpipe. Record the time required for the water level to drop through some increment to a total of 30 cm. Then close valve B, open valves A and V, and allow the water to rise in both standpipes to restore the initial equilibrium conditions.

14.3.2 Calculations. Hydraulic conductivity is calculated with the following equation:

$$K = \frac{r_p^2}{r_c \cdot C} \quad \frac{\Delta h}{\int_0^t hc(t)\, dt}$$

where (see Figure 1)

K = hydraulic conductivity (mm min^{-1}).

r_p = radius of standpipe of inner tube (mm).

r_c = radius of inner tube (mm).

$\Delta h = h_e(t) - h_c(t)$ (mm).

$h_e(t)$ = drop in water level in inner tube under equal level conditions in a time interval of t minutes (mm).

$h_c(t)$ = drop in water level in inner tube under constant outer level conditions in a time interval of t minutes (mm).

C = geometry factor.

The geometry factor C that has been developed by Bouwer (1961) suggests that C is virtually independent of S (Figure 12) if $S/r_c > 3$. Under such conditions, C, as a function of d/r_c only, can be found from Table 4.

14.3.3 Sources of error. As the double tube method makes use of an infiltration surface, the conservation of the original soil structure is of utmost importance. The tubes must also be installed very carefully to prevent leakage from occurring along the tube wall. The application of the equation is conditioned on the infiltration rates remaining constant during the test. Therefore, it is advisable to repeat the equal level infiltration step several times to check on the constancy. Furthermore, the constant outer level step should be done as quickly as possible.

TABLE 4. RELATIONSHIP BETWEEN THE GEOMETRY FACTOR C AND d/r_c FOR THE DOUBLE TUBE METHOD (MODIFIED AFTER BOUWER, 1961)

d/r_c	C
0.10	2.2
0.15	1.9
0.20	1.6
0.30	1.4
0.40	1.2
0.60	1.0
0.80	0.8
1.00	0.7

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METHOD 9131

TOTAL COLIFORM: MULTIPLE TUBE FERMENTATION TECHNIQUE

1.0 Scope and Application

1.1 This method is used to determine the presence of a member of the Coliform group in ground and surface waters.

1.2 The coliform group as analyzed for in this procedure is defined as comprising of all aerobic and facultative anaerobic, gram-negative, nonspore-forming, rod-shaped, bacteria that ferment lactose with gas formation within 48 hours at 35° C.

2.0 Summary of Method

2.1 The Multiple-Tube Fermentation technique is a three-stage procedure in which the results are statistically expressed in terms of the Most Probable Number (MPN). These stages, the presumptive stage, confirmed stage and completed test are briefly summarized below. (For the analysis to be accurate a five-tube test is required.)

2.1.1 Presumptive Stage - A series of lauryl tryptose broth primary fermentation tubes are inoculated with graduated quantities of the sample to be tested. The inoculated tubes are incubated at 35 ± 0.05° C for 24 ± 2 hrs, at which time the tubes are examined for gas formation. For the tubes in which no gas is formed, continue incubation and examine for gas formation at the end of 48 ± 3 hrs. Formation of gas in any amount within 48 ± 3 hrs is a positive presumptive test.

2.1.2 Confirmed Stage - The confirmed stage is used on all primary fermentation tubes showing gas formation during the 24 hour and 48 hour periods. Fermentation tubes containing brilliant green lactose bile broth are inoculated with medium from the tubes showing a positive result in the presumptive test. Inoculation should be performed as soon as possible after gas formation occurs. The inoculated tubes are incubated for 48 ± 3 hrs at 35 ± 0.5° C. Formation of gas at any time in the tube indicates a positive confirmed test.

2.1.3 Completed Test - The completed test is performed on all samples showing a positive result in the confirmed test. It can also be used as a quality control measure on twenty percent of all samples analyzed. One or more plates of eosin methylene blue are streaked with each sample to be analyzed. The streaked plates are incubated for 24 ± 2 hrs at 35 ± 0.5° C.

After incubation transfer 1 or more typical (nucleated, with or without metallic sheen) colonies to a lauryl tryptose broth fermentation tube and a nutrient agar slant. The fermentation tubes and agar slants are incubated at 35 ± 0.5° C for 24 ± 2 hrs or 48 ± 3 hrs if gas is not produced. From the agar slants corresponding to the fermentation tubes in which gas formation occurs, gram stained samples are examined microscopically. The formation of gas in the fermentation tube and the presence of gram-negative, nonspore-forming, rod-shaped bacteria in the agar culture may be considered a satisfactory completed test demonstrating the positive presence of coliform bacteria in the analyzed sample.

2.2 A more detailed treatment of this method is presented in "Standard Methods for the Examination of Water and Wastewaters," 15th Ed. and the EPA manual, "Microbiological Methods for Monitoring the Environment," EPA 600/8-78-017, December, 1978.

3.0 Interference

3.1 The distribution of bacteria in water is irregular. Thus, a 5 tube-test is required in this method for adequate statistical accuracy.

3.2 The presence of residual chlorine or other halogens can prevent the continuation of bacterial action. To prevent this occurrence, sodium thiosulfate should be added to the sterile sample container.

3.3 Water samples high in copper, zinc, or other heavy metals can be toxic. Chelates such as ethylenediaminetetraacetic acid (EDTA) can be used to reduce heavy metal toxicity by adding it to the sterile sample container.

3.4 It is important to keep in mind that MPN tables are probability calculations and inherently have poor precision. They include a 23% positive bias that generally results in high value. The precision of the MPN can be improved by increasing the number of sample portions examined and the number of samples analyzed from the same sampling point.

4.0 Apparatus

4.1 Incubators

Incubators must maintain a uniform and constant temperature at all times in all areas, that is, they must not vary more than ±0.5°C in the areas used. Obtain such accuracy by using a water-jacketed or anhydric-type incubator with thermostatically controlled low-temperature electric heating units properly insulated and located in or adjacent to the walls or floor of the chamber and preferably equipped with mechanical means of circulating air.

Alternatively, use special incubating rooms well insulated and equipped with properly distributed heating units and with forced air circulation, provided that they conform to desired temperature limits. When such rooms are used, record the daily temperature range in areas where plates or tubes are incubated. Provide incubators with open metal wire or sheet shelves so spaced as to assure temperature uniformity throughout the chamber. Leave a 2.5-cm space between walls and stacks of dishes or baskets of tubes.

Maintain an accurate thermometer with the bulb immersed in liquid (glycerine, water, or mineral oil) on each shelf in use within the incubator and record daily temperature readings (preferably morning and afternoon). It is desirable, in addition, to maintain a maximum and minimum registering thermometer within the incubator on the middle shelf to record the gross temperature range over a 24-hour period. At intervals, determine temperature variations within the incubator when filled to maximum capacity. Install a recording thermometer whenever possible, to maintain a continuous and permanent record of temperature.

Keep water depth in the incubator sufficient to immerse tubes to upper level of media.

4.2 Hot-Air Sterilizing Ovens

Use hot-air sterilizing ovens of sufficient size to prevent internal crowding; constructed to give uniform ad adequate sterilizing temperatures of 170 ± 10°C; and equipped with suitable thermometers. Optionally use a temperature-recording instrument.

4.3 Autoclaves

Use autoclaves of sufficient size to prevent internal crowding; constructed to provide uniform temperatures within the chambers (up to and including the sterilizating temperature of 121°C); equipped with an accurate thermometer the bulb of which is located properly on the exhaust line so as to register minimum temperature within the sterilizing chambers (temperature-recording instrument is optional); equipped with pressure gauge and properly adjusted safety valves connected directly with saturated-steam power lines or directly to a suitable special steam generator (do not use steam from a boiler treated with amines for corrosion control); and capable of reaching the desired temperature within 30 min.

Use of a vertical autoclave or pressure cooker is not recommended because of difficulty in adjusting and maintaining sterilization temperature and the potential hazard. If a pressure cooker is used in emergency or special circumstances, equip it with an efficient pressure gauge and a thermometer, the bulb of which is 2.5 cm above the water level.

4.4 Colony Counters

Use Quebec-type colony counter, dark-field model preferred, or one providing equivalent magnification (1.5 diameters) and satisfactory visibility.

4.5 pH Equipment

Use electrometric pH meters, accurate to at least 0.1 pH units, for determining pH values of media.

4.6 Balances

Use balances providing a sensitivity of at least 0.1 g at a load of 150 g, with appropriate weights. Use an analytical balance having a sensitivity of 1 mg under a load of 10 g for weighing small quantitites (less than 2 g) of materials. Single-pan rapid-weigh balances are most convenient.

4.7 Media Preparation Utensils

Use borosilicate glass or other suitable noncorrosive equipment such as stainless steel. Use glassware that is clean and free of residues, dried agar, or other foreign materials that may contaminate media.

4.8 Pipets and Graduated Cylinders

Use pipets of any convenient size, provided that they deliver the required volume accurately and quickly. The error of calibration for a given manufacturer's lot must not exceed 2.5%. Use pipets having graduations distinctly marked and with unbroken tips. Bacteriological transfer pipets or pipets conforming to the APHA standards given in the latest edition of "Standard Methods for the Examination of Dairy Products" may be used. Optimally, protect the mouth end of all pipets by a cotton plug to eliminate hazards to the worker or possible sample contamination by saliva.

Use graduated cylinders meeting ASTM Standards (D-86 and D-216) and with accuracy limits established by the National Bureau of Standards where appropriate.

4.9 Pipet Containers

Use boxes of aluminum or stainless steel, end measurement 5 to 7.5 cm, cylindrical or rectangular, and length about 40 cm. When these are not available, paper wrappings may be substituted. To avoid excessive charring during sterilization, use best-quality sulfate pulp (kraft) paper. Do not use copper or copper alloy cans or boxes as pipet containers.

4.10 Dilution Bottles or Tubes

Use bottles or tubes of resistant glass, preferably borosilicate glass, closed with glass stoppers or screw caps equipped with liners that do not produce toxic or bacteriostatic compounds on sterilization.

Do not use cotton plugs as closures. Mark graduation levels indelibly on side of dilution bottle or tube. Plastic bottles of non-toxic material and acceptable size may be substituted for glass provided that they can be sterilized properly.

4.11 Petri Dishes

Use glass or plastic petri dishes about 100 x 15 mm. Use dishes the bottoms of which are free from bubbles and scratches and flat so that the medium will be of uniform thickness throughout the plate. For the membrance filter technic use loose-lid glass or plastic dishes, 60 x 15 mm, or tight-lid dishes, 50 x 12 mm. Sterilize petri dishes and store in metal cans (aluminum or stainless steel, but not copper), or wrap in paper - preferably best-quality sulfate pulp (kraft) - before sterilizing.

4.12 Fermentation Tubes and Vials

Use only 10 mm x 7 mm fermentation tubes. Where tubes are used for a test of gas production, enclose a shell vial, inverted. Use a vial of such size that it will be filled completely with medium and at lest partly submerged in the tube.

4.13 Inoculating Equipment

Use wire loops made of 22- or 24-gauge nickel alloy (chromel, nichrome, or equivalent) or platinum-iridium for flame sterilization. Single-service transfer loops of aluminum or stainless steel are satisfactory. Use loops at least 3 mm in diameter. Sterilize by dry heat or steam. Single-service hardwood applicators also may be used. Make these 0.2 to 0.3 cm in diameter and at least 2.5 cm longer than the fermentation tube; sterilize by dry heat and store in glass or other nontoxic containers.

5.0 Reagents and Media

5.1 Buffered water: To prepare stock phosphate buffer solution, dissolve 34.0 g potassium dihydrogen phosphate (KH_2PO_4), in 500 ml distilled water, adjust to pH 7.2 ± 0.5 with 1N sodium hydroxide (NaOH), and dilute to 1 liter with distilled water.

Add 1.25 ml stock phosphate buffer solution and 5.0 ml magnesium chloride solution (38 g $MgCl_2$/liter distilled water) to 1 liter distilled water. Dispense in amounts that will provide 99 ± 2.0 ml or 9 ± 0.2 ml after autoclaving for 15 min.

Peptone water: Prepare a 10% solution of peptone in distilled water. Dilute a measured volume to provide a final 0.1% solution. Final pH should be 6.8.

Dispense in amounts to provide 99 ± 2.0 ml or 9 ± 0.2 ml after autoclaving for 15 min.

Do not suspend bacteria in any dilution water for more than 30 min at room temperature because death or multiplication may occur.

5.2 Lauryl Tryptose Broth

Tryptose	20.0 g
Lactose	5.0 g
Dipotassium hydrogen phosphate, K_2HPO_4	2.75 g
Potassium dihydrogen phosphate, KH_2PO_4	2.75 g
Sodium chloride, NaCl	5.0 g
Sodium lauryl sulfate	0.1 g
Distilled water	1 liter

pH should be approximately 6.8 after sterilization. Before sterilization, dispense in fermentation tubes with an inverted vial sufficient medium to cover inverted vial at least partially after sterilization.

Make lauryl tryptose broth of such strength that adding 100-ml or 10-ml portions of sample to medium will not reduce ingredient concentrations below those of the standard medium. Prepare in accordance with Table 1.

TABLE 1. PREPARATION OF LAURYL TRYPTOSE BROTH

Inoculum ml	Amount of Medium in Tube ml	Volume of Medium + Inoculum ml	Dehydrated Lauryl Tryptose Broth Required g/liter
1	10 or more	11 or more	35.6
10	10	20	71.2
10	20	30	53.4
100	50	150	106.8
100	35	135	137.1
100	20	120	213.6

5.3 Brilliant Green Lactose Bile Broth

Peptone	10.0 g
Lactose	10.0 g
Oxgall	20.0 g
Brilliant green	0.0133 g
Distilled water	1 liter

pH should be 7.2 after steriliation. Before sterilization, dispense in fermentation tubes with an inverted vial sufficient medium to cover inverted vial at least partially after sterilization.

5.4 Ammonium Oxalate-Crystal Violet (Hucker's)

Dissolve 2 g crystal violet (90% dye content) in 20 ml 95% ethyl alcohol; dissolve 0.8 g $(NH_4)_2C_2O_4 \cdot H_2O$ in 80 ml distilled water; mix the two solutions and age for 24 hr before use; filter through paper into a staining bottle.

5.5 Lugol's Solution, Gram's Modification

Grind 1 g iodine crystals and 2 g KI in a mortar. Add distilled water, a few milliliters at a time, and grind thoroughly after each addition until solution is complete. Rinse solution into an amber glass bottle with the remaining water (using a total of 300 ml).

5.6 Counterstain

Dissolve 2.5 g safranin dye in 100 ml 95% ethyl alcohol. Add 10 ml to 100 ml distilled water.

5.7 Acetone alcohol

Mix equal volumes of ethyl alcohol, 95%, with acetone.

6.0 Sample Collection, Handling and Presentation

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in the EPA document cited in Section 2 of this method.

6.2 Cleanse all glassware thoroughly with a suitable detergent and hot water, rinse with hot water to remove all trace of residual washing compound, and finally rinse with distilled water. If mechanical glassware washers are used, equip them with influent plumbing of stainless steel or other nontoxic material. Do not use copper piping to distribute distilled water. Use stainless steel or other nontoxic material for the rinse water system.

Sterilize glassware, except when in metal containers, for not less than 60 min at a temperature of 170° C, unless it is known from recording thermometers that oven temperatures are uniform, under which exceptional condition use 160° C. Heat glassware in metal containers to 170° C for not less than 2 hr.

Sterilize sample bottles not made of plastic as above or in an autoclave at 121° C for 15 min.

If water containing residual chlorine and other halogens is to be collected, add sufficient $Na_2S_2O_3$ to clean sample bottle before sterilization to give a concentration about 100 mg/liter in the sample. To a 120-ml bottle add 0.1 ml 10% solution of $Na_2S_2O_3$ (this will neutralize a sample containng about 15 mg/liter residual chlorine). Stopper bottle, cap, and sterilize by either dry or moist heat, as directed previously.

Collect water samples high in copper or zinc and wastewater samples high in heavy metals in sample bottles containing a chelating agent that will reduce metal toxicity. This is particularly significant when such samples are in transit for 4 hr or more. Use 372 mg/liter of the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA). Adjust EDTA solution of pH 6.5 before use. Add EDTA separately to sample bottle before bottle sterilization (0.3 ml 15% solution in a 120-ml bottle) or combine it with the $Na_2S_2O_3$ solution before addition.

6.3 When the sample is collected, leave ample air space in the bottle (at least 2.5 cm) to facilitate mixing by shaking, preparatory to examination. Exercise care to take samples that will be representative of the water being tested and avoid sample contamination at time of collection or in period before examination.

Keep sampling bottle closed until the moment it is to be filled. Remove stopper and hood or cap as a unit, taking care to avoid soiling. During sampling, do not handle stopper or cap and neck of bottle, and protect them from contamination. Hold bottle near base, fill it without rinsing, replace stopper or cap immediately, and secure hood around neck of bottle.

7.0 Procedures

7.1 Procedure for Presumtive Stage (required for MPN analysis):

7.1.1 Inoculate a series of fermentation tubes ("primary" fermentation tubes) with appropriate graduated quantitites (multiples and submultiples of 1 ml) of sample. Be sure that the concentration of nutritive ingredients in the mixture of medium and added sample confoms to the requirements given in Section 5.2. Use a sterile pipet for initial and subsequent transfers from each sample container. If the pipet becomes contaminated before transfers are completed, replace with a sterile pipet. Use a separate sterile pipet for transfers from each different dilution. Do not prepare dilutions in direct sunlight. Use caution when removing sterile pipets from the container; to avoid contamination, do not drag pipet tip across exposed ends of pipets or across lips and necks of dilution bottles. When removing sample, do not insert pipets more than 2.5 cm below the surface of sample or dilution.

When discharging sample portions, hold pipet at an angle of about 45° with tip touching the inside neck of the tube. The portions of sample used for inoculating lauryl tryptose broth fermentation tubes will vary in size and number with the character of the water under examination, but in general use decimal multiples and submultiples of 1 ml. Use Figure 1 as a guide to preparing dilutions. After adding sample, mix thoroughly.

7.1.2 Incubate inoculated fermentation tubes at 35 ± 0.5° C. After 24 ± 2 hr shake each tube gently and examine it and, if no gas has formed and been trapped in the inverted vial, reincubate and reexamine at the end of 48 ± 3 hr. Record presence of absence of gas formation regardless of amount at each examination of the tubes.

7.1.3 Formation of gas in any amount in the inner fermentation tubes or vials within 48 ± 3 hr constitutes a positive Presumptive Test.

Do not confuse the appearance of an air bubble in a clear tube with actual gas production. If gas is formed as a result of fermentation, the broth medium will become cloudy. Active fermentation may be shown by the continued appearance of small bubbles of gas throughout the medium outside the inner vial when the fermentation tube is shaken gently.

The absence of gas formation at the end of 48 ± 3 hr of incubation constitutes a negative test. An arbitrary limit of 48 hr for observation doubtless excludes from consideration occasional members of the coliform group that form gas very slowly and generally are of limited sanitary significance.

7.2 Procedure for Confirmed Stage (required for MPN analysis):

7.2.1 Submit all primary fermentation tubes showing any amount of gas within 24 hr of incubation to the confirmed test. If active fermentation appears in the primary fermentation tube earlier than 24 hr preferably transfer to the confirmatory medium without waiting for the full 24-hr period to elapse. If additional primary fermentation tubes show gas production at the end of 48-hr incubation, submit these to the Confirmed Test.

7.2.1 Gently shake or rotate primary fermentation tube showing gas and, either with a sterile metal loop, 3 mm in diameter, transfer one loopful of culture to a fermentation tube containing brilliant green lactose bile

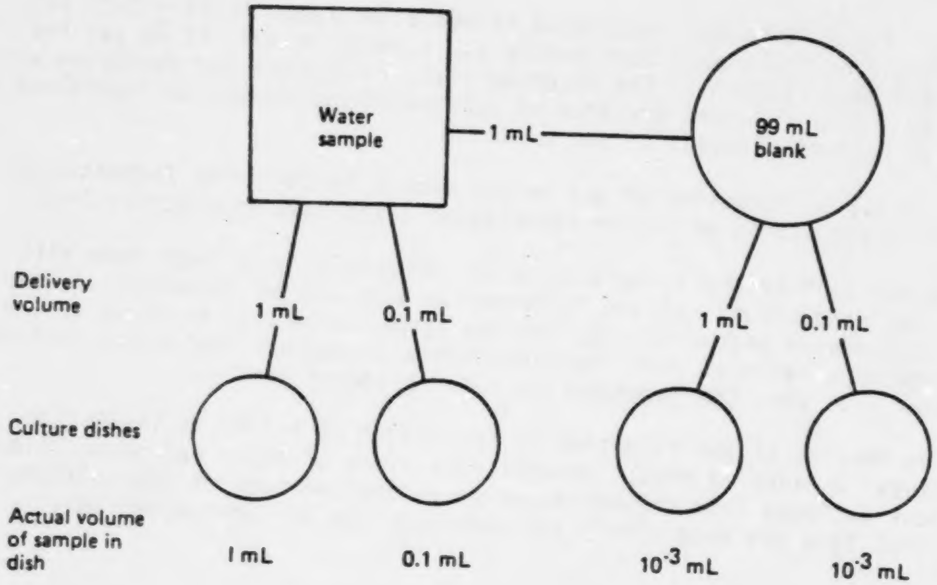

Water sample
1 mL
99 mL blank
Delivery volume
1 mL
0.1 mL
1 mL
0.1 mL
Culture dishes
Actual volume of sample in dish
1 mL
0.1 mL
10-3 mL
10-3 mL

Figure 1. Preparation of dilutions.

broth, or insert a sterile wooden applicator at least 2.5 cm into the culture, promptly remove, and plunge applicator to bottom of fermentation tube containing brilliant green lactose bile broth. Remove and discard applicator.

7.2.3 Incubate the inoculated brilliant green lactose bile broth tube for 48 ± 3 hr at 35 ± 0.5° C. Formation of gas in any amount in the inverted vial of the brilliant green lactose bile broth fermentation tube at any time within 48 ± 3 hr constitutes a positive Confirmed Test.

7.3 Procedure for Completed Test

7.3.1 Use the Completed Test on positive confirmed tubes to establish definitely the presence of coliform bacteria and provide quality control data for twenty percent of all samples analyzed.

7.3.2 Streak one or more eosin methylene blue plates from each tube of brilliant green lactose bile broth showing gas, as soon as possible after the appearance of gas. Streak plates to insure presence of some discrete colonies separated by at least 0.5 cm. Observe the following precautions when streaking plates to obtain a high proportion of successful isolations if coliform organisms are present: (a) use an inoculating needle slightly curved at the tip; (b) tap and incline the fermentation tube to avoid picking up any membrane or scum on the needle; (c) insert end of needle into the liquid in the tube to a depth of approximately 5.0 mm; and (d) streak plate with curved section of the needle in contact with the agar to avoid a scratched or torn surface.

7.3.3 Incubate plates (inverted) at 35 ± 0.5°C for 24 ± 2 hr.

7.3.4 The colonies developing on eosin methylene blue agar are called typical (nucleated, with or without metallic sheen); atypical (opaque, unnucleated, mucoid, pink after 24 hr incubation), or negative all others). From each of these plates pick one or more typical well-isolated coliform colonies or, if no typical colonies are present, pick two or more colonies considered most likely to consist of organisms of the coliform group, and transfer growth from each isolate to a lauryl tryptose broth fermentation tube and to a nutrient agar slant.

If possible, when transferring colonies, choose well-isolated colonies and barely touch the surface of the colony with a flame-sterilized, air-cooled transfer needle to minimize the danger of transferring a mixed culture.

7.3.5 Incubate secondary broth tubes at 35 ± 0.5° C for 24 ± 2 hr; if gas is not produced within 24 ± 2 hr reincubate and examine again at 8 ± 3 hr. Microscopically examine Grain-stained preparations (see Section 7.6) from those 24-hr agar slant cultures corresponding to the secondary tubes that show gas.

7.3.6 Formation of gas in the secondary tube of lauryl tryptose broth within 48 ± 3 hr and demonstration of gram-negative, nonspore-forming, rod-shaped bacteria in the agar culture constitute a satisfactory Completed Test, demonstrating the presence of a member of the coliform group.

7.4 Gram-stain Procedure

7.4.1 Procedure: Prepare a light emulsion of the bacterial growth from an agar slant in a drop of distilled water on a glass slide. Air-dry or fix by passing the slide through a flame and stain for 1 min with the ammonium oxalate-crystal violet solution. Rinse the slide in tap water; apply Lugol's solution for 1 min. (See Sections 5.4 - 5.7 for reagent.)

7.4.2 Rinse the stained slide in tap water. Decolorize for approximtely 15 to 30 sec with acetone alcohol by holding slide between the fingers and letting acetone alcohol flow across the stained smear until no more stain is removed. Do not over-decolorize. Conterstain with safranin for 15 sec, then rinse with tap water, blot dry with bibulous paper, and examine microscopically.

7.4.3 Cells that decolorize and accept the safranin stain are pink and defined as gram-negative in reaction. Cells that do not decolorize but retain the crystal violet stain are deep blue and are defined as gram-positive.

7.5 Computing and Recording of MPN

7.5.1 The calculated density of coliform bacteria in a sample can be obtained from the MPN table, based on the number of positive tubes in each dilution of the Confirmed or Completed Test. Table 2 shows the MPN indices and 95% confidence limits for potable water testing, and Table 3 describes the MPN indice and 95% confidence limits for general use.

7.5.2 Three dilutions are necessary for the determination of the MPN index. For example, in Table 3 if five 10 ml, five 1.0 ml and five 0.1 ml portions of the samples are used as inocula and four of the 10 ml, two of the 1 ml and none of the 0.1 ml of inocula give positive results, the coded result is 4-2-0 and the MPN index is 22 per 100 ml.

7.5.3 In cases when the serial decimal dilution is other than 10, 1 and 0.1 ml, or more than three sample volumes are used in the series, refer to the sources cited in Section 2.2 of this manual for the necessary density determination procedures.

7.5.4 All MPN values for water samples should be reported on the basis of a 100 ml sample.

TABLE 2. MPN INDEX AND 95% CONFIDENCE LIMITS FOR VARIOUS COMBINATIONS OF POSITIVE AND NEGATIVE RESULTS WHEN FIVE 10-ML PORTIONS ARE USED

Number of tubes giving positive reaction out of 5 of 10 ml each	MPN Index per 100 ml	95% Confidence Limits	
		Lower	Upper
0	<2.2	0	6.0
1	2.2	0.1	12.6
2	5.1	0.5	19.2
3	9.2	1.6	29.4
4	16	3.3	52.9
5	>16	8.0	Infinite

TABLE 3. MPN INDEX FOR SERIAL DILUTIONS OF SAMPLE

Number of Tubes Giving Positive Reaction out of			MPN Index per 100 ml	95% Confidence Limits	
5 of 10 ml each	5 of 1 ml each	5 of 0.1 ml each		Lower	Upper
0	0	0	<2		
0	0	1	2	<0.5	7
0	1	0	2	<0.5	7
0	2	0	4	<0.5	11
1	0	0	2	<0.5	7
1	0	1	4	<0.5	11
1	1	0	4	<0.5	11
1	1	1	6	<0.5	15
1	2	0	6	<0.5	15
2	0	0	5	<0.5	13
2	0	1	7	1	17
2	1	0	7	1	17
2	1	1	9	2	21
2	2	0	9	2	21
2	3	0	12	3	28
3	0	0	8	1	19
3	0	1	11	2	25
3	1	0	11	2	25
3	1	1	14	4	34
3	2	0	14	4	34
3	2	1	17	5	46
3	3	0	17	5	46
4	0	0	13	3	31
4	0	1	17	5	46
4	1	0	17	5	46
4	1	1	21	7	63
4	1	2	26	9	78
4	2	0	22	7	67
4	2	1	26	9	78
4	3	0	27	9	80
4	3	1	33	11	93
4	4	0	34	12	93
5	0	0	23	7	70
5	0	1	31	11	89
5	0	2	43	15	110
5	1	0	33	11	93
5	1	1	46	16	120
5	1	2	63	21	150
5	2	0	49	17	130
5	2	1	70	23	170
5	2	2	94	28	220
5	3	0	79	25	190
5	3	1	110	31	250
5	3	2	140	37	340
5	3	3	180	44	500
5	4	0	130	35	300
5	4	1	170	43	490
5	4	2	220	57	700
5	4	3	280	90	850
5	4	4	350	120	1000
5	5	0	240	68	750
5	5	1	350	120	1000
5	5	2	540	180	1400
5	5	3	920	300	3200
5	5	4	1600	640	5800
5	5	5	≥2400		

Source: Microbiological Methods for Monitoring the Environment, EPA 600/18-78-017.

8.0 Quality Control

8.1 Extensive quality control procedures are provided in Part IV of the EPA document cited in Section 2 of this method. These procedures should be adhered to at all times.

8.2 Samples must be maintained as closely as possible to original condition by careful handling and storage. Sample sites and sampling frequency should provide data representative of characteristics and variability of the water quality at that site. Samples should be analyzed immediately. If this is practical they should be refrigerated at a temperature of 1-4° C and analyzed within six hours.

8.3 Quality control of culture media is critical to the validity of microbiological analysis. Some important factors to consider are summarized below:

8.3.1 Order media to last for only one year; always use oldest stock first. Maintain an inventory of all media ordered, including a visual inspection record.

8.3.2 Hold unopened media for no longer than two years. Opened media containers should be discarded after six months.

8.3.3 When preparing media keep containers open as briefly as possible. Prepare media in deionized or distilled water of proven quality. Check the pH of the media after solution and sterilization, it should be within 0.2 units of the stated value. Discard and remake if it is not.

8.3.4 Autoclave media for the minimal time specified by the manufacturer, since the potential for damage increases with increased exposure to heat. Remove sterile media from the autoclave as soon as pressure is zero. Effectiveness of the sterilization should be checked weekly using strips or ampuls of Bacillus stearothemophelus.

8.3.5 Agar plates should be kept slightly open for fifteen minutes after pouring or removal from refrigeration to evaporate free moisture. Plates must be free of lumps, uneven surfaces, pock marks or bubbles which can prevent good contact between the agar and medium.

8.3.6 Avoid shaking fermentation tubes, which can entrap air in the inner vial and produce a false positive result.

8.3.7 Store fermentation tube media in the dark at room temperature or 4° C. If refrigerated incubate overnight at room temperature to detect false positive gas bubbles.

8.3.8 Quality control checks of prepared media should include the incubation of five percent of each batch of medium for two days at 35° C to inspect for growth and positive/negative checks with pure culture.

8.4 Analytical Quality Control Procedures should include:

8.4.1 Duplicate analytical runs on at least 10% of all known positive samples analyzed.

8.4.2 At least one positive control sample should be run each month for each parameter tested.

8.4.3 At least one negative (sterile) control should be run with each series of samples using buffered water and the medium batch used at the beginning of the test series and following every tenth sample. When sterile controls indicate contamination, new samples should be obtained and analyzed.

8.4.4 The water supply used should be periodically checked for contamination by a state laboratory.

8.4.5 For routine MPN tests, at least 5% of the positive confirmed samples should be tested by the complete test.

METHOD 9132

TOTAL COLIFORM: MEMBRANE FILTER TECHNIQUE

1.0 Scope and Application

1.1 This method is used to determine the presence of a member of the Coliform group in waste and groundwater.

1.2 The Coliform group analyzed for in this procedure includes all of the aerobic and facultative anaerobic, gram-negative, nonspore-forming, rod-shaped bacteria that ferment lactose in 24-48 hrs at 35° C.

2.0 Summary of Method

2.1 A predetermined amount of sample is filtered through a membrane filter which retains the bacteria found in the sample.

2.2 In the two-step enrichment procedure the filters containing the bacteria are placed on an absorbent pad saturated with lauryl tryptose broth and incubated at 35° C for 2 hrs. The filters are then transfered to an absorbent pad saturated with M-Endo-media or to a dish containing M-Endo-agar and incubated for another 21 ± 1 hr at 35° C. Sheen colonies are then counted under magnification and reported per 100 ml of original sample.

2.3 An alternative single-step direct technique can also be used. The filter containing the microorganisms is placed directly on the M-Endo-agar or on a pad saturated with M-Endo-broth in a petri dish. The test is then incubated for 24 hrs at 35° C, and sheen colonies are counted.

2.4. A more detailed treatment of this method is presented in "Standard Method for the Examination of Water and Wastewaters", 15th edition, and the EPA manual "Microbiological Methods for Monitoring the Environment," EPA 600/8-78-017, December 1978.

3.0 Interference

3.1 The presence of residual chlorine or other halogen can prevent the continuation of bacterial action. To prevent this occurrence, sodium thiosulfate should be added.

3.2 Water samples high in copper, zinc, or other heavy metals can be toxic. Chelates such as ethylenediaminetetraacetic acid (EDTA) can be used to reduce heavy metal toxicity.

3.3 Turbidity caused by the presence of algae or other interfering material may not permit testing of a sample volume sufficient to yield significant results. Low coliform estimates may be caused by the presence of high numbers of noncoliforms or of toxic substances.

4.0 Apparatus

4.1 Dilution Bottles or Tubes

Use bottles or tubes of resistant glass, preferably borosilicate glass, closed with glass stoppers or screw caps equipped with liners that do not produce toxic or bacteriostatic compounds on sterilization.

Do not use cotton plugs as closures. Mark graduation levels indelibly on side of dilution bottle or tube. Plastic bottles of non-toxic material and acceptable size may be substituted for glass provided that they can be sterilized properly.

4.2 Pipets and Graduated Cylinders

Use pipets of any convenient size, provided that they deliver the required volume accurately and quickly. The error of calibration for a given manufacturer's lot must not exceed 2.5%. Use pipets having graduations distinctly marked and with unbroken tips. Bacteriological transfer pipets or pipets conforming to the APHA standards given in the latest edition of "Standard Methods for the Examination of Dairy Products" may be used. Optimally, protect the mouth end of all pipets by a cotton plug to eliminate hazards to the worker or possible sample contamination by saliva.

Use graduated cylinders meeting ASTM Standards (D-86 and D-216) and with accuracy limits established by the National Bureau of Standards where appropriate.

4.3 Containers for Culture Medium

Use clean borosilicate glass flasks presterilized to reduce bacterial contamination. Any size or shape of flask may be used, but erlenmeyer flasks with metal caps, metal foil covers, or screw caps provide for adequate mixing of the medium contained and are convenient for storage.

4.4 Culture Dishes

Petri-dish type, 60 by 15 mm, 50 x 12 mm, or other appropriate size. The bottom of the dish should be flat and large enough so that the absorbent pad for the culture nutrient will lie flat. Wrap clean culture dishes before sterilization, singly or in convenient numbers, in metal foil if sterilized by dry heat, or suitable paper substitute when autoclaved. If glass petri dishes are used, use borosilicate or equivalent glass. Take precautions to prevent possible loss of medium by evaporation with resultant change in medium concentration, because covers for such dishes are loose-fitting, and to maintain a humid environment for optimum colony development.

Disposable plastic dishes that are tightfitting and meet the specifications noted above also may be used. Suitable sterile plastic dishes are available commercially.

4.5 Filtration Units

The filter-holding assembly (constructed of glass, autoclavable plastic, porcelain, or any noncorrosive bacteriologically inert metal) consists of a seamless funnel fastened by a locking device or held in place by magnetic force or gravity. The design should be such that the membrane filter will be held securely on the porous plate of the receptacle without mechanical damage and all fluid will pass through the membrane during filtration.

Separately wrap the two parts of the assembly in heavy wrapping paper for sterilization by autoclaving and storage until use. Alternatively treat unwrapped parts by ultraviolet radiation before using them. Field units may be sanitized by igniting methyl alcohol or immersing in boiling water for 5 min. Do not ignite plastic parts.

For filtration, mount receptacle of filter-holding assembly in a 1-liter filtering flask with a side tube or other suitable device such that a pressure differential can be exerted on the filter membrane. Connect flask to an electric vacuum pump, a filter pump operating on water pressure, a hand aspirator, or other means of securing pressure differential. Connect an additional flask between filtering flask and vacuum source to trap carry-over water.

4.6 Filter Membranes

Use membrane filters with a rated pore diameter such that there is complete retention of coliform bacteria (0.45 ± 0.02 µm). Use only those filter membranes that have been found, through adequate quality control testing and certification by the manufacturer, to exhibit full retention of the organisms to be cultivated, stability in use, freedom from chemical extractables inimical to the growth and development of bacteria, a satisfactory speed of filtration, no significant influence on medium pH, and no increase in number of confluent colonies or spreaders. Preferably use membranes grid-marked in such a manner that bacterial growth is neither inhibited nor stimulated along the grid lines. Store membrane filters held in stock in an environment without extremes of temperature and humidity. Obtain no more than a year's supply at any one time.

If presterilized membrane filters are to be used, use those for which the manufacturer has certified that the sterilization technic has neither induced toxicity nor altered the chemical or physical properties of the membrane. If membranes are sterilized in the laboratory, remove paper separators - but not the absorbent paper pads - from the packaged filters. Divide filters into groups of 10 to 12, or other convenient units, and place in 10-cm petri dishes or wrap in heavy wrapping paper. Autoclave for 10 min at 121° C. At the end of the sterilization period, let the steam escape rapidly to minimize accumulation of water condensation on filters.

4.7 Absorbent Pads

Absorbent pads consist of disks of filter paper or other material known to be of high quality and free of sulfites or other substances that could inhibit bacterial growth. Use pads approximately 48 mm in diameter and of sufficient thickness to absorb 1.8 to 2.2 ml of medium. Presterilized absorbent pads or pads subsequently sterilized in the laboratory should release less than 1 mg total acidity (calculated as $CaCO_3$) when titrated to the phenolphthalein end point, pH 8.3, using 0.02N NaOH. Where there is evidence of absorbent pad toxicity, pre-soak pads in distilled water at 121° C (in an autoclave) for 15 min, decant the water, and repackage pads in a large petri dish for sterilization and subsequent use. Sterilize pads simultaneously with membrane filters available in resealable kraft envelopes, or separately in other suitable containers. Dry pads so they are free of visible moisture before use. See sterilization procedure described for membrane filters above.

As a substrate substitution for nutrient-saturated absorbent pads, 1.5% agar may be added to the total coliform M-Endo broth medium.

4.8 Forceps

Round-tipped, without corrugations on the inner sides of the tips. Sterilize before use by dipping in 95% ethyl or absolute methyl alcohol and flaming.

4.9 Incubators

Use incubators to provide a temperature of 35 ± 0.5° C and to maintain a high level of humidity (approximately 90% relative humidity).

4.10 Microscope and Light Source

Count membrane filter colonies with a magnification of 10 to 15 diameters and a light source adjusted to give maximum sheen discernment. Optimally use a binocular wide-field dissecting microscope. However, a small fluorescent lamp with magnifier is acceptable. Use cool white fluorescent lamps. Do not use a microscope illuminator with optical system for light concentration from an incandescent light source for coliform colony identification on Endo-type media.

5.0 Reagent

5.1 M-Endo Medium

Tryptose or polypeptone	10.0	g
Thiopeptone or thiotone	5.0	g
Casitone or trypticase	5.0	g
Yeast extract	1.5	g
Lactose	12.5	g
Sodium chloride, NaCl	5.0	g
Dipotassium hydrogen phosphate, K_2HPO_4	4.375	g
Potassium dihydrogen phosphate, KH_2PO_4	1.375	g
Sodium lauryl sulfate	0.050	g
Sodium desoxycholate	0.10	g
Sodium sulfite, Na_2SO_3	2.10	g
Basic fuchsin	1.05	g
Distilled water	1	liter

Rehydrate in 1 liter distilled water containing 20 mL 95% ethanol. Heat to boiling, promptly remove from heat, and cool to below 45° C. Do not sterilize by autoclaving. Final pH should be between 7.1 and 7.3.

Store finished medium in the dark at 2 to 10° C and discard any unused medium after 96 hr.

Note: This medium may be solidified by adding 1.2 to 1.5% agar before boiling.

6.0 Sample Collection, Handling and Presentation

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Cleanse all glassware thoroughly with a suitable detergent and hot water, rinse with hot water to remove all trace of residual washing compound, and finally rinse with distilled water. If mechanical glassware washers are used, equip them with influent plumbing of stainless steel or other nontoxic material. Do not use copper piping to distribute distilled water. Use stainless steel or other nontoxic material for the rinse water system.

Sterilize glassware, except when in metal containers, for not less than 60 min at a temperature of 170° C, unless it is known from recording thermometers that oven temperatures are uniform, under which exceptional condition use 160° C. Heat glassware in metal containers to 170° C for not less than 2 hr.

Sterilize sample bottles not made of plastic as above or in an autoclave at 121° C for 15 min.

For plastic bottles that distort on autoclaving, use low-temperature ethylene oxide gas sterilization. If water containing residual chlorine and other halogens is to be collected, add sufficient $Na_2S_2O_3$ to clean sample bottle before sterilization to give a concentration about 100 mg/liter in the sample. To a 120-ml bottle add 0.1 ml 10% solution of $Na_2S_2O_3$ (this will neutralize a sample containng about 15 mg/liter residual chlorine). Stopper bottle, cap, and sterilize by either dry or moist heat, as directed previously.

Collect water samples high in copper or zinc and wastewater samples high in heavy metals in sample bottles containing a chelating agent that will reduce metal toxicity. This is particularly significant when such samples are in transit for 4 hr or more. Use 372 mg/liter of the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA). Adjust EDTA solution of pH 6.5 before use. Add EDTA separately to sample bottle before bottle sterilization (0.3 ml 15% solution in a 120-ml bottle) or combine it with the $Na_2S_2O_3$ solution before addition.

6.3 When the sample is collected, leave ample air space in the bottle (at least 2.5 cm) to facilitate mixing by shaking, preparatory to examination. Exercise care to take samples that will be representative of the water being tested and avoid sample contamination at time of collection or in period before examination.

Keep sampling bottle closed until the moment it is to be filled. Remove stopper and hood or cap as a unit, taking care to avoid soiling. During sampling, do not handle stopper or cap and neck of bottle, and protect them from contamination. Hold bottle near base, fill it without rinsing, replace stopper or cap immediately, and secure hood around neck of bottle.

6.4 Start bacteriological examination of a water sample promptly after collection to avoid unpredictable changes. If samples cannot be processed within 1 hr after collection, use an iced cooler for storage during transport to the laboratory.

Hold temperature of all stream pollution samples below 10° C during a maximum transport time of 6 hr. Refrigerate these samples upon receipt in the laboratory and process within 2 hr. When local conditions necessitate delays in delivery of samples longer than 6 hr, make field examinations using field laboratory facilities located at the site of collection or use delayed-incubation procedures.

7.0 Procedure

7.1 Selection of Sample Size

7.1.1 Size of sample will be governed by expected bacterial density, which in finished-water samples will be limited only by the degree of turbidity.

7.1.2 An ideal sample volume will yield growth of about 50 coliform colonies and not more than 200 colonies of all types. Examine finished waters by filtering duplicate portions of the same volume, such as 100 to 500 ml or more, or by filtering two diluted volumes. Examine other waters by filtering three different volumes, depending on the expected bacterial density. When less than 20 ml of sample (diluted or undiluted) is filtered, add a small amount of sterile dilution water to the funnel before filtration. This increase in water volume aids in uniform dispersion of the bacterial suspension over the entire effective filtering surface.

7.2 Filtration of Sample

7.2.1 Using sterile forceps, place a sterile filter over porous plate of receptacle, grid side up. Carefully place matched funnel unit over receptacle and lock it in place. Filter sample under partial vacuum. With filter still in place, rinse funnel by filtering three 20- 30- mL portions of sterile dilution water. Unlock and remove funnel, immediately remove filter with sterile forceps, and place it on sterile pad or agar with a rolling motion to avoid entrapment of air.

7.2.2 Use sterile filtration units at the beginning of each filtration series as a minimum precaution to avoid accidental contamination. A filtration series is considered to be interrupted when an interval of 30 min or longer elapses between sample filtrations. After such interruption, treat any further sample filtration as a new filtration series and sterilize all membrane filter holders in use.

7.2.3 Decontaminate this equipment between successive filtrations by use of flowing steam, boiling water; or, if available. an ultraviolet sterilizer. When using the UV sterilation procedure, a [illegible] in exposure to UV radiation is sufficient and should kill 99.9 % of all bacteria. Eye protection is recommended to protect against stray radiation from a non-light tight sterilizatrion cabinent. This UV equipment is not commercially available and is not required, although its use is recommended.

7.3 Two-Step Enrichment Technique

7.3.1 Place a sterile absorbent pad in the upper half of a sterile culture dish and pipet enough enrichment medium (1.8 to 2.0 ml lauryl tryptose broth) to saturate pad. Carefully remove any surplus liquid. Aseptically place filter through which the sample has been passed on pad. Incubate filter, without inverting dish, for 1.5 to 2 hr at 35 ± 0.5° C in an atmosphere of at least 90% relative humidity.

7.3.2 Remove enrichment culture from incubator, lift filter from enrichment pad, and roll it onto the agar surface. Incorrect filter placement is at once obvious, because pathces of unstained membrane indicate entrapment of air. Where such patches occur, carefully reseat filter on agar surface. If the liquid medium is used, prepare final culture by removing enrichment culture from incubator and separating the dish halves. Place a fresh sterile pad in bottom half of dish and saturate it with 1.8 to 2.0 ml of final M-Endo medium. Transfer filter, with same precautions as above, to new pad. Discard used pad.

With either the agar or the liquid medium, invert dish and incubate for 20 to 22 hr at 35 ± 0.5° C. Proceed to Counting (7.4 below).

7.4 Alternative Single-Step Direct Technique

7.4.1 If the agar-based medium is used, place prepared filter directly on agar as described in preceding section and incubate for 22 to 24 hr at 35 ± 0.5° C.

7.4.2 If liquid medium is used, place a pad in the culture dish and saturate with 1.8 to 2.0 ml M-Endo medium. Place prepared filter directly on pad, invert dish, and incubate for 22 to 24 hr at 35 ± 0.5°C.

7.5 Counting

7.5.1 The typical coliform colony has a pink to dark-red color with a metallic surface sheen. The sheen area may vary in size from a small pin-head to complete coverage of the colony surface. Count sheen colonies with the aid of a low-power (10 to 15 magnifications) binocular wide-field dissecting microscope or other optical device, with a cool white fluorescent light source directed above, and as nearly perpendicular as possible to, the.

plane of the filter. The total count of colonies (coliform and noncoliform) on Endo-type medium has no relation to the total number of bacteria present in the original sample and, so far as is known, no significance can be inferred or correlation made with the quality of the water sample.

7.6 Calculation of Coliform Density

7.6.1 Report coliform density as (total) coliforms/100 ml. Compute the count, using membrane filters with 20 to 80 coliform colonies and not more than 200 colonies of all types per membrane, by the following equation:

$$\text{(Total) coliform colonies/100 ml} = \frac{\text{coliform colonies counted} \times 100}{\text{ml sample filtered}}$$

7.6.2 Water of Drinking Water Quality

With water of good quality, the number of coliform colonies will be less than 20 per membrane. In this event, count all coliform colonies and use the formula given above to obtain coliform density.

If confluent growth occurs, that is, growth covering either the entire filtration area of the membrane or a portion thereof, and colonies are not discrete, report results as "confluent growth with or without coliforms." If the total number of bacterial colonies, coliforms plus noncoliforms, exceeds 200 per membrane, or if the colonies are too indistinct for accurate counting, report results as "too numerous to count" (TNTC). In either case, request a new sample and select more appropriate volumes to be filtered per membrane, remembering that the standard drinking water portion is 100 ml. Thus, instead of filtering 100 ml per membrane, 50-ml portions may be filtered through each of two membranes, 25-ml portions may be filtered through each of four membranes, etc. Total the coliform counts observed on the membranes and report as number per 100 ml.

7.6.3 Water of Other than Drinking Water Quality

As with potable water samples, if no filter has a coliform count falling in the ideal range, total the coliform counts on all filters and report as number per 100 ml. For example, if duplicate 50-ml portions were examined and the two membranes had five and three coliform colonies, respectively, report the count as eight coliform colonies per 100 ml, i.e.,

$$\frac{(5 + 3) \times 100}{(50 + 50)}$$

Similarly, if 50-, 25-, and 10-ml portions were examined and the counts were 15, 6, and 1 coliform colonies, respectively, report the count as 25/100 ml, i.e.,

$$\frac{(15 + 6) \times 100}{(50 + 25 + 10)}$$

On the other hand, if 10-, 1.0-, and 0.1-ml portions were examined with counts of 40, 9, and 1 coliform colonies, respectively, select the 10-ml portion only for calculating the coliform density because this filter had a coliform count falling in the ideal range. The result is 400/100 ml, i.e.,

$$\frac{(40 \times 100)}{10}$$

In this last example, if the membrane with 40 coliform colonies also had a total bacterial colony count greater than 200, report the coliform count as 400/100 ml.

Report confluent growth or membranes with colonies too numerous to count as described in 7.6.2 above. Request a new sample and select more appropriate volumes for filtration.

7.6.4 Statistical Reliability of Membrane Filter Results

Although the statistical reliability of the membrane filter technic is greater than that of the MPN procedure, membrane counts really are not absolute numbers. Table 1 illustrates some 95% confidence limits.

TABLE 1. 95% Confidence Limits for Membrane Filter Results Using 100-ml Sample

Number of coliform colonies counted	95% Confidence Limits	
	Lower	Upper
1	0.05	3.0
2	0.35	4.7
3	0.81	6.3
4	1.4	7.7
5	2.0	9.2

8.0 Quality Control

8.1 Extensive quality control procedures are provided in Part IV of the EPA document cited in Section 2 of this method. These procedures should be adhered to at all times.

8.2 Samples must be maintained as closely as possible to original condition by careful handling and storage. Sample sites and sampling frequency should provide data represntative of characteristics and variability of the water quality at that site. Samples should be analyzed immediately. If this is practical they should be refrigerated at a temperature of 1-4° C and analyzed within six hours.

8.3 Quality control of culture media is critical to the validity of microbiological analysis. Some important factors to consider are summarized below:

8.3.1 Order media to last for only one year; always use oldest stock first. Maintain an inventory of all media ordered, including a visual inspection record.

8.3.2 Hold unopened media for no longer than two years. Opened media containers should be discarded after six months.

8.3.3 When preparing media keep containers open as briefly as possible. Prepare media in deionized or distilled water of proven quality. Check the pH of the media after solution and sterilization, it should be within 0.2 units of the stated value. Discard and remake if it is not.

8.3.4 Autoclave media for the minimal time specified by the manufacturer, since the potential for damage increases with increased exposure to heat. Remove sterile media from the autoclave as soon as pressure is zero. Effectiveness of the sterilization should be checked weekly using strips or ampuls of Bacillus stearothemophelus.

8.3.5 Agar plates should be kept slightly open for fifteen minutes after pouring or removal from refrigeration to evaporate free moisture. Plates must be free of lumps, uneven surfaces, pock marks or bubbles which can prevent good contact between the agar and medium.

8.3.6 Quality control checks of prepared media should include the incubation of five percent of each batch of medium for two days at 35° C to inspect for growth and positive/negative checks with pure culture.

8.4 Analytical quality control procedures should include:

8.4.1 Duplicate analytical runs on at least 10% of all known positive samples analyzed.

8.4.2 At least one positive control sample should be run each month for each parameter tested.

8.4.3 At least one negative (sterile) control should be run with each series of samples using buffered water and the medium batch used at the beginning of the test series and following every tenth sample. When sterile controls indicate contamination, new samples should be obtained and analyzed.

8.4.4 The water supply used should be periodically checked for contamination by a state laboratory.

8.5 Quality Control Specifications for Membrane Filters

8.5.1 Membrane filters can be purchased sterile or packaged for sterilization. They can be sterilized by autoclaving, ethylene oxide or irradiation. Membrane manufacturers should certify that their membranes meet stated specifications on sterility, retention, recovery, pore size, flow rate, pH, total acidity, phosphate and other extractables.

8.5.2 Membrane performance should be tested to assure proper results. Each lot ordered should be inspected for proper shape, gridlines, diffusability and correct colony development. Membranes containing sizable areas with no colony development are questionable.

METHOD 9200

NITRATE

1.0 Scope and Application

1.1 This method is applicable to the analysis of ground, drinking, surface and saline waters, and domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentration is 0.1 to 2 mg NO_3-N/liter.

2.0 Summary of Method

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100° C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3.0 Interferences

3.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color present not due to dissolved organics.

3.2 If the sample is colored or the conditions of the test cause extraneous coloration, this interference should be corrected by running a concurrent sample under the same conditions in the absence of the brucine sulfanilic acid reagent.

3.3 Strong oxidizing or reducing agents cause intereference. The presence of oxidizing agents may be determined by a residual chlorine test; reducing agents may be detected with potassium permanganate.

3.3.1 Oxidizing agents interference is eliminated by the addition of sodium arsenite.

3.3.2 Reducing agents may be oxidized by addition of H_2O_2.

3.4 Ferrous and ferric iron and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/liter these are negligible.

3.5 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

4.0 Apparatus

4.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.

4.2 Sufficient number of 40-50 ml glass sample tubes for reagent blanks, standards, and samples.

4.3 Neoprene coated wire racks to hold sample tubes.

4.4 Water bath suitable for use at 100° C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without significant drop in temperature when the tubes are immersed.

4.5 Water bath suitable for use at 10-15° C.

5.0 Reagents

5.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

5.2 Sodium chloride solution (30%): Dissolve 300 g NaCl in distilled water and dilute to 1 liter.

5.3 Sulfuric acid solution: Carefully add 500 ml conc. H_2SO_4 to 125 ml distilled water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

5.4 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate -- $(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O$ -- and 0.1 g sulfanilic acid $(NH_2C_6H_4SO_3H \cdot H_2O)$ in 70 ml hot distilled water. Add 3 ml conc. HCl, cool, mix and dilute to 100 ml with distilled water. Store in a dark bottle at 5° C. This solution is stable for several months; the pink color that develops slowly does not affect its usefulness. Mark bottle with warning CAUTION: Brucine Sulfate is toxic; take care to avoid ingestion.

5.5 Potassium nitrate stock solution: 1.0 ml = 0.1 mg NO_3-N. Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml chloroform per liter. This solution is stable for at least 6 months.

5.6 Potassium nitrate standard solution: 1.0 ml = 0.001 mg NO_3-N. Dilute 10.0 ml of the stock solution (5.5) to 1 liter in a volumetric flask. This standard solution should be prepared fresh weekly.

5.7 Acetic acid (1 + 3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of distilled water.

5.8 Sodium hydroxide (1 N): Dissolve 40 g of NaOH in distilled water. Cool and dilute to 1 liter.

6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4° C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H_2SO_4 per liter) and refrigerated.

7.0 Procedure

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (5.7) or sodium hydroxide (5.8). If necessary, filter to remove turbidity. Sulfuric acid can be used in place of acetic acid if preferred.

7.2 Set up the required number of sample tubes in the rack to handle reagent blank, standards and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, a set of duplicate samples must be run to which all reagents except the brucine-sulfanilic acid have been added.

Add 0.5 ml brucine sulfanilic acid reagent (5.4) to each tube (except the interference control tubes, 5.3) and carefully mix by swirling, then place the rack of tubes in the 100° C water bath for exactly 25 minutes.

Caution: Immersion of the tube rack into the bath should not decrease the temperature of the bath more than 1 to 2° C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.4 Pipette 10.0 ml of standards and samples or an aliquot of the samples diluted to 10.0 ml into the sample tubes.

7.5 If the samples are saline, add 2 ml of the 30% sodium chloride solution (5.2) to the reagent blank, standards and samples. For fresh water samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold water bath (0-10° C).

7.6 Pipette 10.0 ml of sulfuric acid solution (5.3) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Remove rack of tubes from the hot water bath and immerse in the cold water bath and allow to reach thermal equilibrium (20-25° C).

7.8 Read absorbance against the reagent blank at 410 nm using a 1 cm or longer cell.

7.9 Calculation

7.9.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg NO_3-N/1. (The color reaction does not always follow Beer's law.)

7.9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg NO_3-N/1. Multiply by an appropriate dilution factor if less than 10 ml of sample is taken.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A set of standards must be included with each batch of samples.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Analyze check standards after approximately every 15 samples.

8.5 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.6 Spiked samples or standard reference materials shall be employed with each batch to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 Precision and Accuracy

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.16	0.092	-6.79	-0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

METHOD 9250

CHLORIDE (COLORIMETRIC, AUTOMATED FERRICYANIDE AAI)

1.0 Scope and Application

1.1 This automated method is applicable to ground, drinking, surface, and saline waters, and domestic and industrial wastes. The applicable range is 1 to 250 mg Cl/liter.

2.0 Summary of Method

2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.

3.0 Interferences

3.1 No significant interferences.

4.0 Apparatus

4.1 Technicon Auto Analyzer consisting of:

4.1.1 Sampler I.

4.1.2 Continuous filter.

4.1.3 Manifold.

4.1.4 Proportioning pump.

4.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.

4.1.6 Recorder.

5.0 Reagents

5.1 Ferric Ammonium Sulfate: Dissolve 60 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in approximately 500 ml distilled water. Add 355 ml of conc. HNO_3 and dilute to 1 liter with distilled water. Filter.

5.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of $Hg(SCN)_2$ in 1 liter of distilled water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.

5.3 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140° C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.

5.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested.

ml of Stock Solution	Conc., mg/l
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0
50.0	250.0

Choose 3 of the 9 standard concentrations, in such a way that the chosen standards will bracket the expected concentration range of the sample.

6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 No special requirements for preservation.

7.0 Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one distilled water intake line.

7.2 Allow both colorimeter and recorder to warm up to 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

7.6 Calculation.

7.6.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

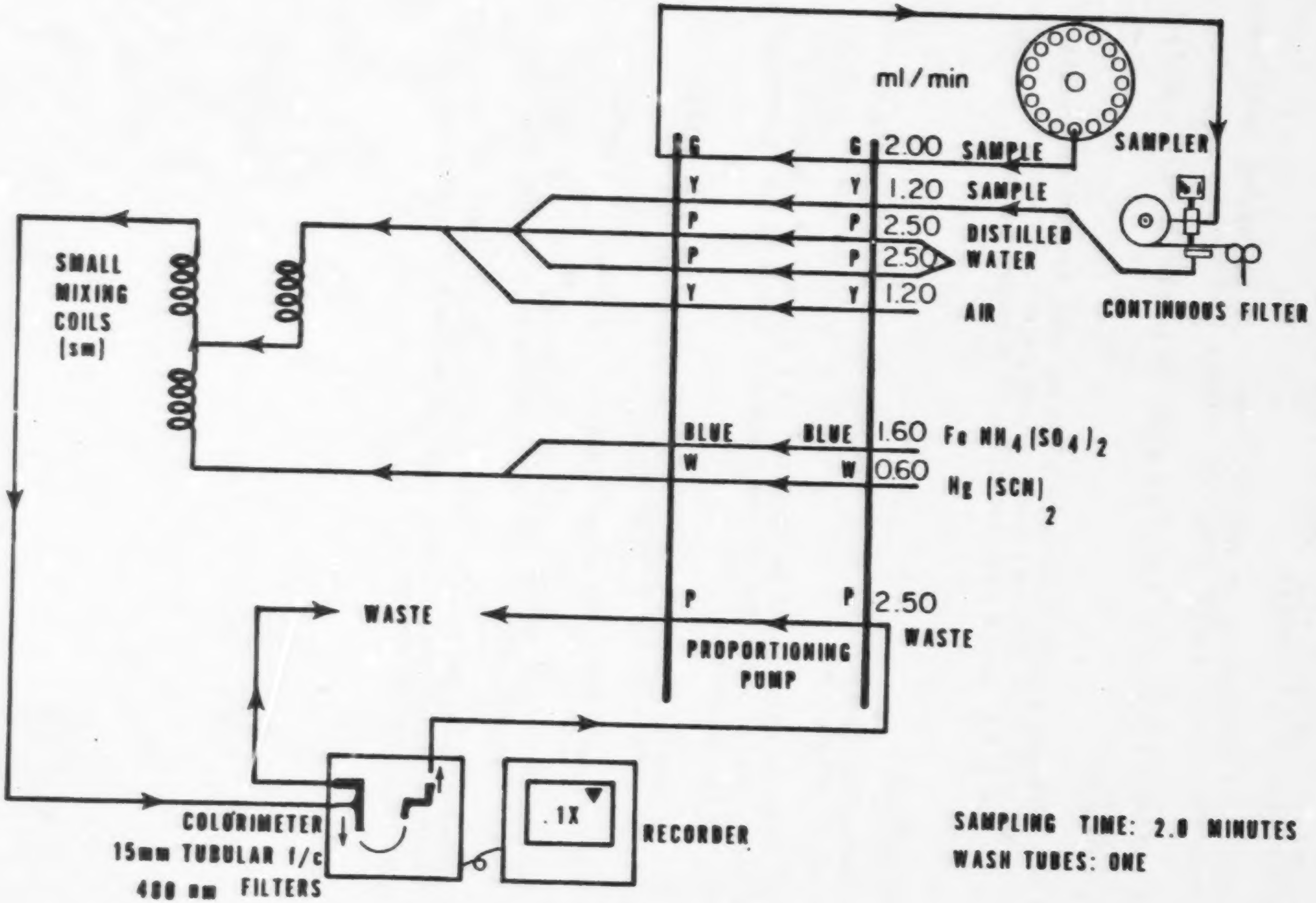
8.2 Calibration curves must be composed of a minimum of a blank and three standards. Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Analyze check standards after approximately every 15 samples.

8.5 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.6 Spiked samples or standard reference materials shall be employed with each batch to ensure that correct procedures are being followed and that all equipment is operating properly.


ml / min
SAMPLER
CONTINUOUS FILTER
G
G
2.00 SAMPLE
Y
Y
1.20 SAMPLE
P
P
2.50 DISTILLED WATER
P
P
2.50
Y
Y
1.20 AIR
BLUE
BLUE
1.60 Fe NH4 (SO4)2
W
W
0.60 Hg (SCN)2
P
P
2.50 WASTE
PROPORTIONING PUMP
WASTE
SMALL MIXING COILS (sm)
COLORIMETER
15mm TUBULAR f/c
400 nm FILTERS
.1X
RECORDER

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. CHLORIDE MANIFOLD AA-I

METHOD 9251

CHLORIDE (COLORIMETRIC, AUTOMATED FERRICYANIDE AAII)

1.0 Scope and Application

1.1 This automated method is applicable to ground, drinking, surface, and saline waters, and domestic and industrial wastes. The applicable range is 1 to 200 mg Cl/liter.

2.0 Summary of Method

2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.

3.0 Interferences

3.1 No significant interferences.

4.0 Apparatus

4.1 Technicon Auto Analyzer consisting of:

4.1.1 Sampler I.

4.1.2 Analytical cartridge.

4.1.3 Proportioning pump.

4.1.4 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.

4.1.5 Recorder.

4.1.6 Digital printer (optional).

5.0 Reagents

5.1 Mercuric thiocyanate solution: Disoolve 4.17 gm of $Hg(SCN)_2$ in 500 ml of methanol. Dilute to 1 liter with methanol, mix and filter through filter paper.

5.2 Ferric nitrate solution, 20.2%: Dissolve 202 gm $(Fe(NO_3)_3 \cdot 9\ H_2O$ in 500 ml of distilled water. Add 31.5 ml conc nitric acid, mix and dilute to 1 liter with distilled water. A combined color reagent is also available from Technicon.

5.3 Color reagent: Add 150 ml of mercuric thiocyanate solution (5.1) to 150 ml of ferric nitrate solution (5.2), mix, and dilute to 1 liter with distilled water.

5.4 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140° C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.

5.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested.

ml of Stock Solution	Conc., mg/liter
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0

Choose 3 of the 9 standard concentrations in such a way that the chosen standard will bracket the expected concentration range of the sample.

6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 No special requirements for preservation.

7.0 Procedure

7.1 Where particulate matter is present, the sample must be filtered prior to the determination. This can be accomplished by having the Technicon continuous filter as an integral part of the system. The sample may be centrifuged in place of filtration.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.

7.3 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.4 When a stable baseline has been obtained, start the sampler.

7.5 Calculation.

7.5.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Analyze check standards after approximately every 15 samples.

8.5 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.6 Spiked samples or standard reference materials shall be employed with each batch to ensure that correct procedures are being followed and that all equipment is operating properly.

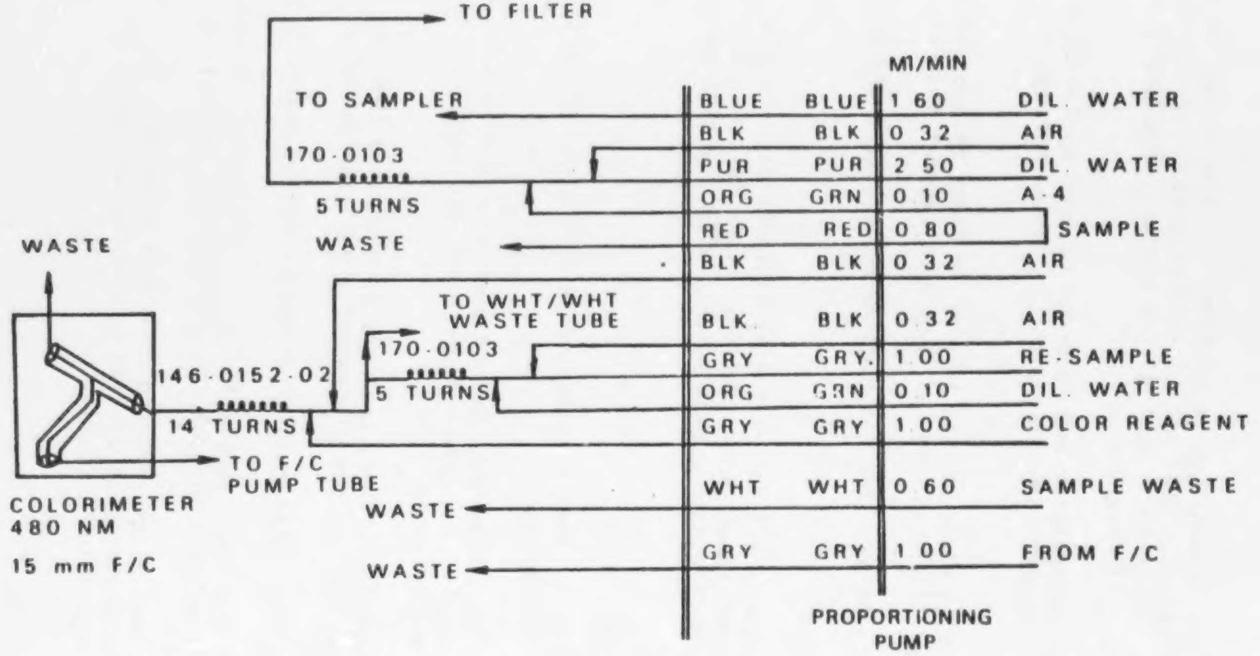

TO FILTER
Ml/MIN
TO SAMPLER
170-0103
5 TURNS
WASTE
WASTE
TO WHT/WHT WASTE TUBE
170-0103
5 TURNS
146-0152-02
14 TURNS
TO F/C PUMP TUBE
COLORIMETER
480 NM
15 mm F/C
WASTE
WASTE
BLUE BLUE 1.60 DIL. WATER
BLK BLK 0.32 AIR
PUR PUR 2.50 DIL. WATER
ORG GRN 0.10 A-4
RED RED 0.80 SAMPLE
BLK BLK 0.32 AIR
BLK. BLK 0.32 AIR
GRY GRY. 1.00 RE-SAMPLE
ORG GRN 0.10 DIL. WATER
GRY GRY 1.00 COLOR REAGENT
WHT WHT 0.60 SAMPLE WASTE
GRY GRY 1.00 FROM F/C
PROPORTIONING PUMP

FIGURE 1
CHLORIDE MANIFOLD AA 11

METHOD 9252

CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)

1.0 Scope and Application

1.1 This method is applicable to ground, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml is used.

1.3 Automated titration may be used.

2.0 Summary of Method

2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.0 Interferences

3.1 Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain waste, problems may occur.

3.2 Sulfite interference can be eliminated by oxidizing the 50 ml of sample solution with 0.5 to 1 ml of H_2O_2.

4.0 Apparatus

4.1 Standard laboratory titrimetric equipment including 1 ml or 5 ml microburet with 0.01 ml graduations.

5.0 Reagents

5.1 Standard sodium chloride, 0.025 N: Dissolve 1.4613 g ± 0.0002 g of sodium chloride (dried at 600° C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark.

5.2 Nitric acid, HNO_3 solution (3 + 997).

5.3 Sodium hydroxide solution, NaOH, (10 g/liter).

5.4 Hydrogen perioxide (30%), H_2O_2.

5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 ml volumetric and dilute to the mark.

5.6 Mercuric nitrate titrant (0.141 N): Dissolve 24.2 g $Hg(NO_3)_2 \cdot H_2O$ in 900 ml of distilled water acidified with 5.0 ml conc. HNO_3 in a 1-liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 7. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 ml aliquot is equivalent to 5.00 mg of chloride.

5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 ml of distilled water acidified with 0.5 ml conc. HNO_3 (sp. gr. 1.42) in a 1-liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 7. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2 \cdot H_2O$ in 25 ml of distilled water acidified with 0.25 ml of conc. HNO_3 (sp. gr. 1.42) in a 1-liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 7. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 ml aliquot is equivalent to 500 ug of chloride.

5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 ml 95% ethanol in a 100-ml volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.

5.10 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in a 100-ml volumetric and dilute to the mark with 95% ethanol or isopropanol.

6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 No special requirements for preservation.

7.0 Procedure

7.1 Place 50 ml of sample in a vessel for titration. If the concentration is greater than 20 mg/liter chloride, use 0.141 N mercuric nitrate titrant (5.6) in step 7.6 or dilute. If the concentration is less than 2.5 mg/liter of chloride, use 0.0141 N mercuric nitrate titrant (5.8) in step 7.6, a 1-ml or 5-ml microburet, and determine an indicator blank on 50 ml chloride-free water using procedure 7.6. If the concentration is less than 0.1 mg/liter of chloride, concentrate an appropriate volume to 50 ml.

7.2 Add 5 to 10 drops of mixed indicator reagent (5.9), shake or swirl solution.

7.3 If a blue-violet or red color appears add HNO_3 solution (5.2) dropwise until the color changes to yellow.

7.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.2) dropwise until the color changes to blue violet; then add HNO_3 solution.

7.5 Add 1 ml excess HNO_3 solution (5.2) dropwise until the color changes to yellow.

7.6 Titrate with mercuric nitrate until a blue-violet color persists throughout the solution. See 7.1 for choice of titrant normality. Alphazurine indicator solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

7.6.1 If chromate is present at <100 mg/liter and iron is not present, add 5 to 10 drops of alphazurine indicator solution (5.10) and acidify to pH3 (indicating paper). End point will then be an olive-purple color.

7.6.2 If chromate is present at >100 mg/liter and iron is not present, add 2 ml of fresh hydroquinone solution (5.5).

7.6.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 ml fresh hydroquinone solution (5.5).

7.6.4 If sulfite ion is present, add 0.5 ml of H_2O_2 solution (5.4) to 50 ml sample and mix for 1 minute.

Calculation

$$\text{mg chloride/liter} = \frac{(A - B)N \times 35{,}450}{\text{ml of sample}}$$

where

A = ml titrant for sample
B = ml titrant for blank
N = normality mercuric nitrate titrant

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplication sample is a sample brought through the whole sample preparation process.

8.5 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 Precision and Accuracy

9.1 Forty-two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride mg/liter	Precision as Standard Deviation mg/liter	Accuracy as Bias, %	Bias, mg/liter
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

9.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/l, the standard deviation was ±1.0.

9.3 A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

METHOD 9310

GROSS ALPHA AND GROSS BETA

1.0 Scope and Application

1.1 This method covers the measurement of gross alpha and gross beta particle activities in surface and groundwaters.

1.2 The method is applicable to the measurement of alpha emitters having energies above 3.9 megaelectronvolts (MeV) and beta emitters having maximum energies above 0.1 MeV.

1.3 The minimum limit of concentration to which this method is applicable depends on sample size, counting system characteristics, background, and counting time.

1.4 Since, in this method for gross alpha and gross beta measurement, the radioactivity of the sample is not separated from the solids of the sample, the solids concentration is very much a limiting factor in the sensitivity of the method for any given water sample. Also, for samples with very low concentrations of radioactivity, it is essential to analyze as large a sample aliquot as is needed to give reasonable counting times.

1.5 The largest sample aliquot that should be counted for gross alpha activity is that size aliquot which gives a solids density thickness of 5 mg/cm^2 in the counting planchet. For a 2-inch diameter counting planchet (20 cm^2), an aliquot containing 100 mg of nitrated dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross alpha activity.

1.6 When the concentration of total solids (TS) is known for a given water sample and the alpha background and the counting efficiency of a given counting system are known, the counting time that is needed to meet the required sensitivity (3 pCi/liter) can be determined by equations given in Appendix C.

1.7 For the counting of gross beta activity in a water sample the TS is not as limiting as for gross alpha activity because beta particles are not stopped in solids as easily as are alpha particles. Very often a single sample aliquot is evaporated and counted for both gross alpha and gross beta activity. In that case the sample aliquot size would be dictated by the solids limitations for alpha particles. For water samples that are to be counted for gross beta activity, equations in Appendix C can also be used to determine the necessary counting time to meet a sensitivity for gross beta activity (4 pCi/l).

1.8 Radionuclides that are volatile under the sample preparation conditions of this method will not be measured. In some areas of the country the nitrated water solids (sample evaporated with nitric acid present) will not remain at a constant weight after being dried at 105°C for two hours and then exposed to the atmosphere before and during counting. Other radioactivities may also be lost during the sample evaporation and drying at 105°C (such as some chemical forms of radioiodine). Those types of water samples need to be heated to a dull red heat for a few minutes to convert the salts to oxides. Sample weights are then usually sufficiently stable to give consistent counting rates and a correct counting efficiency can then be assigned. Some radioactivities, such as the cesium radioisotopes, may be lost when samples are heated to dull red color. Such losses are limitations of the test method.

1.9 This method provides a rapid screening measurement to indicate whether specific analyses are required.

When the gross alpha particle activity exceeds 5 pCi/l, the same or an equivalent sample shall be analyzed for alpha-emitting radium isotopes (Method 9315) or an alternative measurement of radium-226 alpha emission ("Standard Methods for the Examination of Water and Wastewater," 15th Edition, Method 705 or 706). Gross beta particle emissions exceeding 15 pCi/l in a sample shall be analyzed for Strontium-89 and Cesium-134 ("Standard Methods for the Examination of Water and Wastewater," 15th Edition, Methods 704 and 709, respectively). If gross beta activity exceeds 50 pCi/l, the identity of the major radioactive constituents must be evaluated and the appropriate organ and total body doses determined.

2.0 Summary of Method

2.1 An aliquot of a preserved water sample is evaporated to a small volume and transferred quantitatively to a tared 2-inch stainless steel counting planchet. The sample residue is dried to constant weight, reweighed to determine dry residue weight, then counted for alpha and/or beta radioactivity.

2.2 Counting efficiencies for both alpha and beta particle activities are selected according to the amount of sample solids from counting efficiency vs. sample solids standard curves.

3.0 Interferences

3.1 Moisture absorbed by the sample residue is an interference as it obstructs counting and self-absorption characteristics. If a sample is counted in an internal proportional counter, static charge on the sample residue can cause erratic counting, thereby preventing an accurate count.

3.2 Non-uniformity of the sample residue in counting planchet interferes with the accuracy and precision of the method.

3.3 Sample density on the planchet area should be not more than 10 mg/cm^2 for gross alpha and not more than 20 mg/cm^2 for gross beta.

3.4 When counting alpha and beta particle activity by a gas flow proportional counting system, counting at the alpha plateau discriminates against beta particle activity, whereas counting at the beta plateau is sensitive to alpha particle activity present in the sample. This latter effect should be determined and compensated for during the calibration of the specific instrument being used.

4.0 Apparatus (See Appendix D for details and specifications.)

4.1 Gas-flow proportional counting system, or

4.2 Scintillation detection system,

4.3 Stainless steel counting planchets,

4.4 Electric hot plate,

4.5 Drying oven,

4.6 Drying lamp

4.7 Glass desiccator

4.8 Glassware

4.9 Analytical balance

5.0 Reagents

All chemicals should be of "reagent-grade" or equivalent whenever they are commercially available.

5.1 Distilled or deionized water having a resistance value between 0.5 and 2.0 megaohms (2.0 to 0.5 mhos)/cm at 25°C.

5.2 Nitric acid, $1\underline{N}$: Mix 6.2 ml $16\underline{N}$ HNO_3 (conc.) with deionized or distilled water and dilute to 100 ml.

6.0 Sample Handling and Preservation

6.1 All samples must have been collected in a manner which addresses the considerations discussion in Section One of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15 ml 1N HNO_3 per liter of sample is usually sufficient.) If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

6.3 The container choice should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.0 Procedure

7.1 Calibrations

7.1.1. For absolute gross alpha and gross beta measurement, the detectors must be calibrated to obtain the ratio of count rate to disintegration rate. Americium-241 (used for alpha activity in the collaborative test of this method) has higher alpha particle energy and radium-226 radionuclides but is close to the energy of the alpha particles emitted by naturally occurring thorium-228 and radium-224. Standards should be prepared in the geometry and weight ranges to be encountered in these gross analyses. It is, therefore, the prescribed radionuclide for gross alpha calibration. NBS or NBS-traceable americium-241 is available from Standard Reference Materials Catalog, NBS Special Publications 260, U.S. Department of Commerce (1976), and from Quality Assurance Branch, EMSL-LV, P.O. Box 15027, Las Vegas, Nevada 89114.

7.1.2 Strontium-90 and cesium-137 have both been used quite extensively as standards for gross beta activity. Standard solutions of each of these radionuclides are readily available. Cesium is volatile at elevated temperatures (above 450°C). Some water supplies have dissolved solids (salts) that, when converted to nitrate salts, are quite hygroscopic and need to be converted to oxides by heating to red heat to obtain sample aliquots that are weight-stable. Sample weight stability is essential to gross alpha and gross beta measurements to ensure the accuracy of the self-absorption counting efficiency factor to be used for the samples. Strontium-90 in equilibrium with its daughter yttrium-90 is the prescribed radionuclide for gross beta calibrations.

7.1.3 For each counting instrument to be used, the analyst should prepare separate alpha and beta particle self-absorption graphs showing water sample residue weight (mg) vs. the efficiency factor (cpm/dpm), using standard alpha and beta emitter solutions and tap water. For the alpha graph standard, alpha activity is added to varying size aliquots of tap water, such that the aliquot residue weight is varied between 0 and 100 mg (for a 2-inch counting planchet). A similar graph is prepared with standard beta activity and tap water aliquots, varying the residue weight between 0 and 300 mg (for a 2-inch planchet). If it is planned to use water sample aliquot volumes that always contain 100 mg of dried water solids, then only the efficiency factor for that residue weight needs to be established.

7.1.4 Tap water aliquots with added americium-241 or strontium-90 standard, should be acidified with a few ml 16N HNO_3, evaporated to a small volume in a beaker on a hot plate, transferred quantitatively in 5 ml portions or less to a tared counting planchet, evaporated to dryness, and finally dried at 105°C for 1 hour (or flamed to a red heat if dried solids appear to be noticeably hygroscopic). Weight-stable aliquot residues should then be alpha and/or beta counted until at least 10,000 total counts have been accumulated. A single set of reference standards prepared in this way can be used for each counting instrument for separate graph preparations and can be stored for reverification whenever needed.

7.2 Transfer to a beaker an aliquot of water sample of a volume that contains no more than 100 mg (for alpha only or alpha and beta determination) or 200 mg (for beta only determination) of total water solids. Evaporate the aliquot to near dryness on a hot plate. If water samples are know or suspected to contain chloride salts, those chloride salts should be converted to nitrate salts before the sample residue is transferred to a stainless steel planchet (chlorides will attack stainless steel and increase the sample solids and no correction can be made for those added solids). Chloride salts can be converted to nitrate salts by adding 5 ml portions of 16N HNO_3 to the sample residue and evaporating to near dryness. (Two treatments are usually sufficient.) Add 10 ml 1N HNO_3 to the beaker and swirl to dissolve the residue. Quantitatively transfer the aliquot concentrate in small portions (not more than 5 ml at a time) to a tared planchet, evaporating each portion to dryness.

7.3 Dry the sample residue in a drying oven at 105°C for at least 1 hour, cool in a desiccator, weigh, and count. Store the sample residue in a desiccator until ready for counting.

7.4 Some types of water dissolved solids, when converted to nitrate salts, are quite hygroscopic even after being dried at 105°C for 1 hour. When such hygroscopic salts are present with samples that are put into an automatic counting system, those samples gain weight while they are waiting to be counted and inaccurate counting data result. When there is evidence of hygroscopic salts in sample counting planchets, it is recommended that they be flamed to a dull red heat with a Meeker burner for a few minutes to convert the nitrate salts to oxides before weighing and counting. (It is possible to have a loss of cesium during the flaming of the samples).

Hours from separation to counting	Ingrowth correction factor
0	1.00
1	1.02
2	1.04
3	1.06
4	1.08
5	1.10
6	1.12
24	1.49
48	1.91
72	2.25
96	2.54
120	2.78
144	2.99
192	3.29
240	3.51

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.4 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

D = beta efficiency factor, read from graph of efficiency versus mg of water solids per cm^2 of planchet area, (cpm/dpm),

V = volume of sample aliquot, (ml), and

2.22 = conversion factor from dpm/pCi

7.6.3 When counting beta radioactivity in the presence of alpha radioactivity by gas-flow proportional counting systems (at the beta plateau) alpha particles are also counted. Since alpha particles are more readily absorbed by increasing sample thickness than beta particles, the alpha/beta count ratios vary with increasing sample thickness. Therefore, it is necessary to prepare a calibration curve by counting standards containing americium-241 with increasing thickness of solids on the alpha plateau and then on the beta plateau, plotting the ratios of the two counts vs. density thickness. The alpha amplification factor (E) from that curve is used to correct the amplified alpha count on the beta plateau. When significant alpha activity is indicated by the sample count at the alpha voltage plateau, the beta activity of the sample can be determined by counting the sample at the beta voltage plateau and calculating the activity from the following equation:

$$\text{Beta (pCi/liter)} = \frac{(B - AE) \times 1000)}{2.22 \times D \times V}$$

where:

B = (as defined above)

D = (as defined above)

A = (as defined above)

E = alpha amplification factor, read from the graph of the ratio of alpha counted at the beta voltage/alpha counted at the alpha voltage vs. sample density thickness, and

V = volume of sample aliquot, (ml), and

2.22 = conversion factor from dpm/pCi

7.7 Errors associated with the results of the analysis should also be reported.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination is occurring.

8.3 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.4 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

METHOD 9315

ALPHA-EMITTING RADIUM ISOTOPES

1.0 Scope and Application

1.1 This method covers the measurement of the total soluble alpha emitting radioisotopes of radium, namely radium-223, radium-224, and radium-226 in surface and groundwaters.

1.2 Although the method does not always give an accurate measurement of the radium-226 content of the sample (when other radium alpha emitters are present), it can be used to screen samples. When the total radium alpha activity of a drinking water sample is greater than 5 pCi/l, then the radium-226 analysis is required. If the level of radium-226 exceeds 3 pCi/l, the sample must also be measured for radium 228 (Method 9320).

1.3 Since this method provides for the separation of radium from other water dissolved solids in the sample, the sensitivity of the method is a function of sample size, reagent and instrument background, counting efficiency, and counting time.

1.4 Absolute measurement can be made by calibrating the alpha detector with standard radium-226 in the geometry obtained with the final precipitate.

2.0 Summary of Method

2.1 The radium in the surface water or groundwater sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Citric acid is added to the water sample to assure that complete interchange occurs before the first precipitation step. The final $BaSO_4$ precipitate which includes radium-226, radium-224 and radium-223 is alpha counted to determine the total disintegration rate of the radium isotopes.

2.2 The radium activities are counted in an alpha counter where efficiency for determining radium-226 has been calibrated with a standard of known radium-226 activity. By making a correction for the ingrowth of alpha activity in radium-226 for the elapsed time after separation, one can determine radium activity in the sample. Since some daughter ingrowth can occur before the separated radium is counted, it is necessary to make activity corrections for the count rate. A table of ingrowth factors for various times after radium separation is provided. (See Section 7.14.)

3.0 Interferences

3.1 Inasmuch as the radiochemical yield of the radium activity is based on the chemical yield of the $BaSO_4$ precipitate, the presence of significant natural barium in the sample will result in a falsely high chemical yield.

3.2 Radium isotopes are separated from other alpha emitting radionuclides by this method.

3.3 The alpha count of the separated radium must be corrected for its partially ingrown alpha emitting daughters.

4.0 Apparatus

4.1 Alpha scintillation or a gas-flow proportional alpha particle counting system with low background (<1 cpm).

4.2 Stainless steel counting planchets

4.3 Electric hot plate

4.4 Drying oven and/or drying lamp

4.5 Glass desiccator

4.6 Analytical balance

4.7 Centrifuge

4.8 Glassware

5.0 Reagents

5.1 Distilled or deionized water.

5.2 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp. gr. 1.05, 99.8%.

5.3 Ammonium Sulfate, 200 mg/ml: Dissolve 20g $(NH_4)_2SO_4$ in a minimum of water and dilute to 100 ml.

5.4 Barium carrier, 16 mg/ml, standardized: Dissolve 2.846g $BaCl_2 \cdot 2H_2O$ in water, add 0.5 ml 16 N HNO_3 and dilute to 100 ml with water.

Standardization: (in triplicate)

Pipette 2.0 ml carrier solution into a centrifuge tube containing 15 ml water. Add 1 ml 18N H_2SO_4 with stirring and digest precipitate in a water bath for 10 minutes. Cool, centrifuge, and decant the supernatant. Wash precipitate with 15 ml water. Transfer the precipitate to a tared stainless steel planchet with a minimum of water. Dry under infra-red lamp, store in desiccator and weigh as $BaSO_4$.

5.5 Citric acid, 1M: Dissolve 19.2g $C_6H_8O_7 \cdot H_2O$ in water and dilute to 100 ml.

5.6 EDTA reagent, basic (0.25M): Dissolve 20g NaOH in 750 ml water, heat and slowly add 93g disodium ethylenedinitriloacetate dihydrate, ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$). Heat and stir until dissolved, filter through coarse filter paper and dilute to 1 liter.

5.7 Lead carrier, 15 mg/ml: Dissolve 2.397g $Pb(NO_3)2$ in water, add 0.5 ml 16N HNO_3 and dilute to 100 ml with water.

5.8 Sodium hydroxide, 6N: Dissolve 24 g NaOH in 80 ml water and dilute to 100 ml.

5.9 Sulfuric acid, 18N: Cautiously mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of water.

5.10 Sulfuric acid, 0.1N: Mix 1 volume 18N H_2SO_4 with 179 volumes of water.

6.0 Sample Handling and Preservation

6.1 All samples must have been collected in a manner which addresses the considerations discussion in Section One of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15 ml 1N HNO_3 per liter of sample is usually sufficient.) If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

6.3 The container choice should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.0 Procedure

7.1 Calibrations

7.1.1 The counting efficiency for radium alpha particles with barium sulfate carrier present must be determined using a standard (known) radium alpha activity and 32 mg of barium carrier as $BaSO_4$ (same carrier amount used in samples). This is done with spiked distilled water samples and the procedure for regular samples is followed. Note the time of the Ra-$BaSO_4$ precipitation.

7.1.2 The radium alpha counting efficiency, E, is calculated as follows:

$$E\ (\text{cpm/dpm}) = \frac{C}{A \times I}$$

where:

C = sample net cpm (gross counts minus background divided by the counting time in minutes).

A = dpm of radium-226 added to sample.

I = ingrowth factor for the elapsed time from Ra-$BASO_4$, precipitation to mid-point of counting time.

7.2 To a 1000-ml surface water or groundwater sample, add 5 ml 1M $C_6H_8O_7 \cdot H_2O$, 1 ml lead carrier, and 2.0 ml barium carrier, and heat to boiling.

7.3 Cautiously, with vigorous stirring, add 20 ml 18N H_2SO_4. Digest 5 to 10 minutes and let the mixed $BaSO_4$-$PbSO_4$ precipitate settle overnight. Decant and discard supernate.

7.4 Transfer the precipitate to a centrifuge tube with a minimum amount of 0.1N H_2SO_4. Centrifuge and discard supernate.

7.5 Wash the precipitate twice with 0.1N H_2SO_4. Centrifuge and discard washes.

7.6 Dissolve the precipitate by adding 15 ml basic EDTA reagent; heat in a hot water bath and add a few drops 6N NaOH until solution is complete.

7.7 Add 1 ml $(NH_4)_2SO_4$ (200 mg/ml) and stir thoroughly. Add 17.4N CH_3COOH dropwise until precipitation begins, then add 2 ml extra. Digest 5 to 10 minutes.

7.8 Centrifuge, discard the supernate, and record time.

Note: At this point, the separation of the $BaSO_4$ is complete and the radon (and daughters) ingrowth commences.

7.9 Wash the $BaSO_4$ precipitate with 15 ml water, centrifuge, and discard wash.

7.10 Transfer the precipitate to a tared stainless-steel planchet with a minimum of water, and dry under infra-red lamps.

Note: Drying should be rapid but not too vigorous to minimize any loss of radon-222 that has already grown into the precipitate.

7.11 Cool, weigh, and store in desiccator.

7.12 Count in a gas-flow internal proportional counter or an alpha scintillation counter to determine the alpha activity.

7.13 Calculation

7.13.1 Calculate the radium-226 concentration, D, (which would include any radium-224 and radium-223 that is present) in picocuries per liter as follows:

$$D = \frac{C}{2.22 \times EVR \times I}$$

where:

C = net count rate, cpm,

E = counter eficiency, for radium-226 in $BaSO_4$ predetermined for this procedure (see Sec. 7.1.2).

V = liters of sample used,

R = fractional chemical yield,

I = ingrowth correction factor (See Sec 7.1.4), and

2.22 = conversion factor from dpm/pCi.

7.14 It is not always possible to count the $BaSO_4$ precipitate immediately after separation, therefore, corrections must be made for the ingrowth of the radium-226 daughters between the time of separation and counting according to the following table:

7.5 Count for alpha and beta activity at their respective voltage plateaus. If the sample is to be recounted for reverification, store it in a desiccator.

Note: As long as counting chambers are capable of handling the same size planchet, alpha and beta activity can be determined at their respective voltage plateaus in the designated counting instruments. Keep planchet in the desiccator until ready to count because vapors from moist residue can damage detector and window and can cause erratic measurements. If the gas-flow internal proportional counter does not discriminate for the higher energy alpha pulses at the beta plateau, the alpha activity must be subtracted from the beta plus alpha activity. This is particularly important for samples with high alpha activity.

7.6 Calculations

7.6.1 Calculate the alpha radioactivity by the following equation:

$$\text{Alpha (pCi/liter)} = \frac{A \times 1000}{2.22 \times C \times V}$$

where:

A = net alpha count rate (gross alpha count rate minus the background count rate) at the alpha voltage plateau,

C = alpha efficiency factor, read from graph of efficiency versus mg of water solids per cm^2 of planchet area, (cpm/dpm),

V = volume of sample aliquot, (ml), and

2.22 = conversion factor from dpm/pCi

7.6.2 Calculate the beta radioactivity by the following equations.

7.6.2.1 If there are no significant alpha counts when the sample is counted at the alpha voltage plateau, the beta activity can be determined from the following equation:

$$\text{Beta (pCi/liter)} = \frac{B \times 1000}{2.22 \times D \times V}$$

where:

B = net beta count rate (gross alpha count rate minus the background count rate at the beta voltage plateau),

METHOD 9320

RADIUM-228

1.0 Scope and Application

1.1 This method covers the measurement of radium-228 in groundwater and, if desired, the determination of radium-226 on the same sample. If the level of radium-226 is above 3 pCi/liter, the sample must also be measured for radium-228.

1.2 This technique is devised so that the beta activity from actinium-228 which is produced by decay of radium-228, can be determined and related to the radium-228 that is present in the sample.

1.3 To quantify actinium-228 and thus determine radium-228, the efficiency of the beta counter for measuring the very short half-lived actinium-228 (avg. beta energy-0.404 keV) is to be calibrated with a beta source of comparable average beta energy.

2.0 Summary of Method

2.1 The radium in the water sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Both radium-226 and radium-228 are collected in this manner. After a 36-hour ingrowth of actinium-228 from radium-228, the actinium-228 is carried on yttrium oxalate, purified and beta counted. If radium-226 is also desired, the activity in the supernate can be reserved for coprecipitation on barium sulfate, dissolving in EDTA and storing for ingrowth in a sealed radon bubbler.

3.0 Interferences

3.1 As evidenced from the results of the performance studies, the presence of strontium-90 in the water sample gives a positive bias to the radium-228 activity measured. However, strontium-90 is not likely to be found in groundwater except possibly in monitoring wells around a radioactive burial site.

3.2 Excess barium in the water sample might result in a falsely high chemical yield.

4.0 Apparatus

4.1 Gas-flow proportional counting system. (Low-background beta <3 cpm).

4.2 Electric hot plate.

4.3 Centrifuge

4.4 Membrane filters, matricel 47mm

4.5 Drying lamp

4.6 Glassware

4.7 Stainless steel counting planchets

4.8 Analytical balance

5.0 Reagents

5.1 Distilled or deionized water.

5.2 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp. gr. 1.05, 99.8%.

5.3 Ammonium hydroxide, 15N: NH_4OH (conc.), sp gr. 0.90, 56.6%.

5.4 Ammonium oxalate, 5%: Dissolve 5g $(NH_4)_2C_2O_4 \cdot H_2O$ in water and dilute to 100 ml.

5.5 Ammonium sulfate, 200 mg/ml: Dissolve 20g $(NH_4)_2SO_4$ in water and dilute to 100 ml.

5.6 Ammonium sulfide, 2%: Dilute 10 ml $(NH_4)_2S$, (20-24%), to 100 ml with water.

5.7 Barium carrier, 16 mg/ml, standardized: Dissolve 2.846 g $BaCl_2$; $2H_2O$ in water, add 0.5 ml 16 N HNO_3 and dilute to 100 ml with water.

5.8 Citric acid, 1M: Dissolve 19.2g $C_6H_8O_7 \cdot H_2O$ in water and dilute to 100 ml.

5.9 EDTA reagent, basic (0.25M): Dissolve 20g NaOH in 750 ml water, heat and slowly add 93g disodium ethylenedinitriloacetate dehydrate, ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) while stirring. After the salt is in solution, filter through coarse filter paper and dilute to 1 liter.

5.10 Lead carrier, 15 mg/ml: Dissolve 2.397g $Pb(NO_3)_2$ in water, add 0.5 ml 16N HNO_3 and dilute to 100 ml with water.

5.11 Lead carrier, 1.5 mg/ml: Dilute 10 ml lead carrier, (15 mg/ml), to 100 ml with water.

6.0 Sample Handling and Preservation

6.1 All samples must have been collected in a manner which addresses the considerations discussion in Section One of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15 ml 1N HNO_3 per liter of sample is usually sufficient.) If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15 ml 1N HNO_3 per liter of sample is usually sufficient.) If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

6.3 The container choice should be plastic over glass to prevent loss due to breakage during transportation and handling.

7.0 Procedure

7.1 Calibrations

7.1.1 Counter efficiency: The beta counter may be calibrated with actinium-228 or strontium-89 ($t_{1/2}$ = 51d). Strontium-89 has an average beta energy of 0.589 KeV, while the average beta energy for actinium-228 is 0.404 KeV. A standard strontium-89 tracer solution can be used to determine beta efficiencies over a range of precipitate weights on the stainless steel planchet.

7.2 For each liter of water, add 5 ml 1M $C_6H_8O_7 \cdot H_2O$ and few drops methyl orange indicator. The solution should be red.

Note: At the time of sample collection add 2 ml 16N HNO_3 for each liter of water.

7.3 Add 10 ml lead carrier (15 mg/ml), 2 ml strontium carrier (10 mg/ml), 2.0 ml barium carrier (16 mg/ml), and 1 ml yttrium carrier (18 mg/ml); stir well. Add 15N NH_4OH until a definite yellow color is obtained, then add a few drops excess. Heat to incipient boiling and maintain at this temperature for 30 minutes.

7.4 Precipitate lead and barium sulfates by adding 18N H_2SO_4 until the red color reappears, then add 0.25 ml excess. Add 5 ml $(NH_4)_2SO_4$ (200 mg/ml) for each liter of sample. Stir frequently and keep at a temperature of about 90°C for 30 minutes.

7.5 Cool slightly, then filter with suction through a 47-mm metricel membrane filter (GA6,0.45 μ-pore size). Make a quantitative transfer of precipitate to the filter by rinsing last particles out of beaker with a strong jet of water.

7.6 Carefully place filter with precipitate in the bottom of a 250-ml beaker. Add about 10 ml 16N HNO_3 and heat gently until the filter completely dissolves. Transfer the precipitate into a polypropylene centrifuge tube with additional 16N HNO_3. Centrifuge and discard supernate.

7.7 Wash the precipitate with 15 ml 16N HNO_3, centrifuge, and discard supernate. Repeat this washing a second time.

7.8 Add 25 ml basic EDTA reagent, heat in a hot water bath, and stir well. Add a few drops 10N NaOH if the precipitate does not readily dissolve.

7.9 Add 1 ml strontium-yttrium mixed carrier and stir thoroughly. Add a few drops 10N NaOH if any precipitate forms.

7.10 Add 1 ml $(NH_4)_2SO_4$ (200 mg/ml) and stir thoroughly. Add 17.4N CH_3COOH until barium sulfate precipitates, then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate.

7.11 Add 20 ml basic EDTA reagent, heat in a hot water bath, and stir until precipitate dissolves. Repeat steps 8.9 and 8.10. (Note time of last barium sulfate precipitation; this is the beginning of the actinium-228 in growth time.)

7.12 Dissolve the precipitate in 20 ml basic EDTA reagent as before, then add 1.0 ml yttrium carrier (9 mg/ml) and 1 ml lead carrier (1.5 mg/ml). If any precipitate forms, dissolve by adding a few drops 10N NaOH. Cap the polypropylene tube and age at least 36 hours.

7.13 Add 0.3 ml $(NH_4)_2S$ and stir well. Add 10N NaOH dropwise with vigorous stirring until lead sulfide precipitates, then add 10 drops excess. Stir intermittently for about 10 minutes. Centrifuge and decant supernate into a clean tube.

7.14 Add 1 ml lead carrier (1.5 mg/ml), 0.1 ml $(NH_4)_2S$, and a few drops 10N NaOH. Repeat precipitation of lead sulfide as before. Centrifuge and filter supernate through Whatman #42 filter paper into a clean tube. Wash filter with a few ml water. Discard residue.

7.15 Add 5 ml 18N NaOH, stirwell and digest in a hot water bath until yttrium hydroxide coagulates. Centrifuge and decant supernate into a beaker. Save for barium yield determination, step 7.20 (Note time of yttrium hydroxide precipitation; this is the end of the actinium-228 ingrowth time and beginning of actinium-228 decay time.)

7.16 Dissolve the precipitate in 2 ml 6N HNO_3. Heat and stir in as hot water bath about 5 minutes. Add 5 ml water and reprecipitate yttrium hydroxide with 3 ml 10N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and add this supernate to the supernate produced in step 7.15 in order to determine barium yield.

7.17 Dissolve precipitate with 1 ml 1N HNO_3 and heat in hot water bath a few minutes. Dilute to 5 ml and add 2 ml 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat to coagulate, centrifuge, and discard supernate.

7.18 Add 10 ml water, 6 drops 1N HNO_3 and 6 drops 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat and stir in a hot water bath a few minutes. Centrifuge and discard supernate.

7.19 To determine yttrium yield, transfer quantitatively to a tared stainless steel planchet with a minimum amount of water. Dry under an infra-red lamp to a constant weight and count in a low-background beta counter.

7.20 To the supernate from step 7.15, add 4 ml 16N HNO_3 and 2 ml $(NH_4)_2SO_4$ (200 mg/ml), stirring well after each addition. Add 17.4N CH_3COOH until barium sulfate precipitates, then add 2 ml excess. Digest on a hot plate until precipitate settles. Centrifuge and discard supernate.

7.21 Add 20 ml basic EDTA reagent, rest in a hot water bath, and stir until precipitate dissolves. Add a few drops 10N NaOH if precipitate does not readily dissolve.

7.22 Add 1 ml $(NH_4)_2SO_4$ (200 mg/ml) and stir thoroughly. Add 17.4N CH_3COOH until barium sulfate precipitates, then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate.

7.23 Wash precipitate with 10 ml water. Centrifuge and discard supernate.

7.24 Transfer precipitate to a tared stainless steel planchet with a minimum amount of water. Dry under an infra-red lamp and weigh for barium yield determination.

7.25 Calculation

7.25.1 Calculate the radium-228 concentration, D, in picocuries per liter as follows:

$$D = \frac{C}{2.22 \times EVR} \times \frac{\lambda t_2}{(1-e^{-\lambda t_2})^*} \times \frac{1}{(1-e^{-\ t_3})} \times \frac{1}{e^{-\ t_1}}$$

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* $\frac{\lambda t_2}{(1-e^{-\lambda t_2}}$ is a factor to correct the average count rate to count rate at beginning of counting time.

where:

C = average net count rate, cpm,

E = counter eficiency, for actinium-228, or comparable beta energy nuclide

V = liters of sample used,

R = fractional chemical yield of yttrium carrier (step 7.19) multiplied by fractional chemical yeild of barium carrier (step 7.24).

2.22 = conversion factor from disintegrations/minute to picocuries,

λ = the decay constant for actinium-228 (0.001884 min^{-1}),

t_1 = the time interval (In minutes) between the first yttrium hydroxide precipitation in step 7.15 and the start of the counting time,

t_2 = the time interval of counting in minutes, and

t_3 = the ingrowth time of actinium-228 in minutes measured from the last barium sulfate precipitation in step 7.11 to the first yttrium hydroxide precipitation in step 7.15.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.4 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

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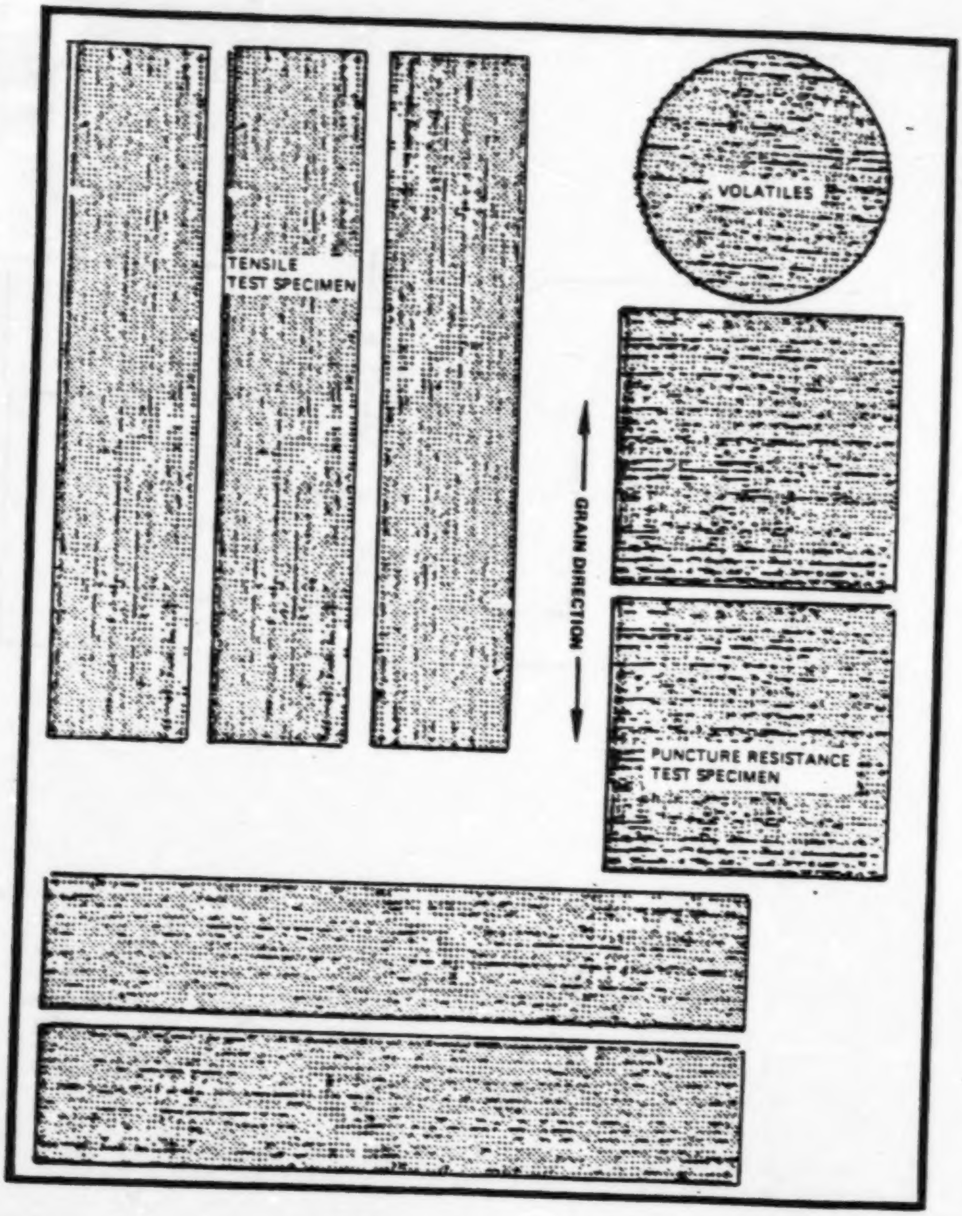
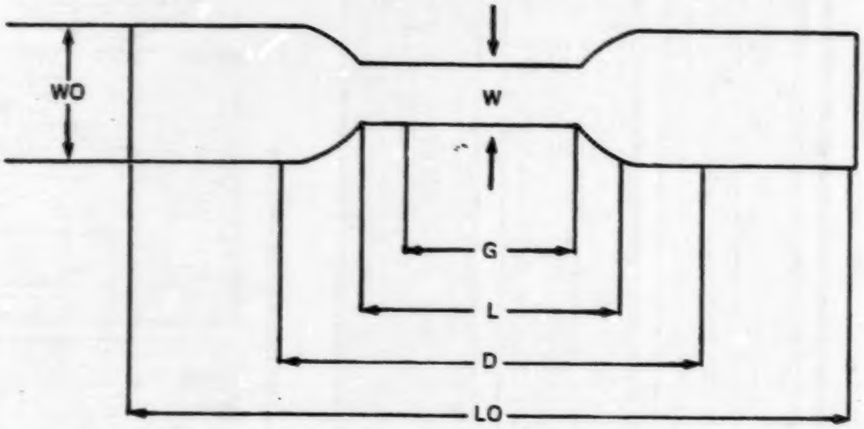

VOLATILES
TENSILE
TEST SPECIMEN
GRAIN DIRECTION
PUNCTURE RESISTANCE
TEST SPECIMEN

Figure 2. Suggested pattern for cutting test specimens from fabric reinforced liner materials. Note: To avoid edge effects, cut specimens 1/8 - 1/4 inch in from edge of immersed sample.



W	-	Width of narrow section	0.25 inches
L	-	Length of narrow section	1.25 inches
WO	-	Width overall	0.625 inches
LO	-	Length overall	3.50 inches
G	-	Gage length	1.00 inches
D	-	Distance between grips	2.00 inches

Figure 3. Die for tensile dumbbell (nonreinforced liners) having the following dimensions.

7.3 Cut pieces of the lining material of a size to fit sample holder, and of a sufficient number to permit at least three samples for each waste and each exposure period. Inspect all samples for flaws and discard unsatisfactory ones. Liner materials with fabric reinforcement require close inspection to ensure that threads of the samples are evenly spaced and straight. The threads in the two directions should cross as close as possible at 90° . Measure the following:

1. Gauge thickness, mil or mm - average of the four corners.
2. Mass, g - to one-hundredth of a gram.
3. Length, cm - average of the lengths of the two sides.
4. Width, cm - average of the widths of the two ends.

Do not cut these samples into the shapes shown in Figures 1 or 2 at this time. Samples will be cut into these shapes, as specified in 7.7, after exposure to the waste fluid.

7.4 Label the test specimens and hang in samples of the waste fluid. (It is recommended that different liner materials be immersed in separate tanks to avoid exchange of plasticizers and soluble constituents when plasticized membranes are being tested.) Expose the test specimens to the stirred waste fluid held at 50±2° C.

7.5 At the end of 30, 60, 90, and 120 days of exposure, remove sufficient specimens from waste fluid to determine the membrane's physical properties (see 7.6 and 7.7). Place wet specimen in a labeled container of fresh waste fluid at room temperature for 1 hr to effect cooling period before testing. Wipe off as much waste as possible and rinse well with water. Place wet specimen in a labeled polyethylene bag to prevent the specimen from drying out. The specimen should be tested within 24 hr of removal from the immersion.

7.6 To test the immersed specimen, wipe off any remaining waste and rinse with dionized water. Blot specimen dry and measure the following.

1. Gauge thickness, mil or mm.
2. Mass, g.
3. Length, cm.
4. Width, cm.

7.7 Perform the following tests on the exposed specimens. Tests for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. See Figure 1 for cutting patterns for non-reinforced liners, and Figure 2 for cutting patterns for reinforced liners.

1. Tear resistance, machine and transverse directions, two specimens each direction for materials without fabric reinforcement.
2. Puncture resistance, two specimens, FTMS 101B, Method 2065. See Figure 1 or 2, as applicable, for sample cutting patterns.
3. Tensile properties, machine and transverse directions, three specimens each direction. See Table 1 for appropriate test method, the recommended test specimen and speed of test, and the values to be reported.
4. Hardness, Duro A (Duro D if Duro A reading is greater than 80), ASTM D2240.

See Figures 1 and 2 for suggested cutting patterns.

7.8 Results and reporting

7.8.1 Plot the curve for each property over the time period 0 to 120 days.

7.8.2 Report all raw, tabulated, and plotted data. Evaluation of the results is described in the documents listed under 6.1, and related agency guidance manuals.

8.0 Quality Control

8.1 Determine the mechanical properties of identical nonimmersed and immersed specimens in accordance with the standard methods for the specific physical property test. Conduct mechanical property tests on nonimmersed and immersed specimens prepared from the same sample or lot of material in the same manner and run under identical conditions. Test immersed specimens immediately after they are removed from the room temperature test solution.

TABLE 2. POLYMERS USED IN FLEXIBLE MEMBRANE LINERS

Thermoplastic Materials (TP)

CPE (Chlorinated polyethylene)[a]
Family of polymers produced by chemical reaction of chlorine on polyethylene. The resulting thermoplastic elastomers contain 25 to 45% chlorine by weight and 0 to 25% crystallinity.

CSPE (Chlorosulfonated polyethylene)[a]
Family of polymers that are produced by polyethylene reacting with chlorine and sulfur dioxide and usually containing 25 to 43% chlorine and 1.0 to 1.4% sulfur.

EIA (Ethylene interpolymer alloy)[a]
A blend of EVA and polyvinyl chloride resulting in a thermoplastic elastomer.

PVC (Polyvinyl chloride)[a]
A synthetic thermoplastic polymer made by polymerizing vinyl chloride.

PVC-CPE (Polyvinyl chloride - chlorosulfonated polyethylene alloy)[a]
A blend of polyvinyl chloride and chlorosulfonated polyethylene.

TN-PVC (Thermoplastic nitrile-polyvinyl chloride)[a]
An alloy of thermoplastic unvulcanized nitrile rubber and polyvinyl chloride.

Vulcanized Materials (XL)

Butyl rubber[a]
A synthetic rubber based on isobutylene and a small amount of isoprene to provide sites for vulcanization.

EPDM (Ethylene propylene diene monomer)[a,b]
A synthetic elastomer based on ethylene, propylene, and a small amount of nonconjugated diene to provide sites for vulcanization.

CM (Crosslinked chlorinated polyethylene)[a]
See chlorinated polyethylene.

CO, ECO (Epichlorohydrin polymers)[a]
Synthetic rubber including two epichlorohydrin-based elastomers which are saturated, high molecular weight aliphatic polyethers with chloromethyl side chains. The two types include homopolymer (CO and a copolymer of epichlorohydrin and ethylene oxide (ECO).

CR (Polychloroprene)[a]
Generic name for a synthetic rubber based primarily on chlorobutadiene.

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[a] Also supplied reinforced with fabric.

[b] Also supplied as a thermoplastic.

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TABLE 2. (Continued)

Partially Crystalline Materials (CX)

HDPE (High density polyethylene)
A polymer prepared by the low-pressure polymerization of ethylene as the sole monomer.

HDPE-A (High density polyethylene/rubber alloy)
A blend of high-density polyethylene and rubber.

PE-EP-A (Polyethylene ethylene/propylene alloy)
A blend of polyethylene and poly(ethylene/porpylene).

T-EPDM (Thermoplastic EPDM)
An ethylene-propylene diene monomer blend resulting in a thermoplastic elastomer.
